ARTIFICIAL SILK

AND ITS MANUFACTURE

BY

JOSEPH FOLTZER

FABRIQUE DE SOIE ET DE CUIR ARTIFICIELS, RIEDIKON-USTER
SWITZERLAND

Translated from the French by

T. WOODHOUSE, F.T.I.

TEXTILE EXPERT AND HEAD OF THE WEAVING AND DESIGNING
DEPARTMENT, DUNDEE TECHNICAL COLLEGE AND SCHOOL OF ART

PREFACE

It is gratifying to note that this standard work on artificial silk is still meeting with favour, and evidently filling its place in textile literature.

About fifty more pages have been added to this edition, so as to include information on dyeing, printing, hydro-extracting, and drying of the material.

The estimated production of artificial silk or rayon for the present year is about 250,000,000 lb., and hence the industry appears to be firmly established.

Since the book now contains particulars relating to more branches of the industry, it should be more valuable as a reference book and as a textbook.

THOMAS WOODHOUSE.

TRANSLATOR'S PREFACE TO SECOND EDITION

SINCE the publication of the First English Edition of this work, the annual production of artificial silk has been approximately doubled, and there is no indication that the rate of increase is diminishing. A large quantity is being used in the weaving industry, and among the newer applications, which are constantly increasing in number, those in the knitting industry are the most noteworthy. Many beautiful effects are produced by dyeing fabrics composed of different kinds of artificial silk yarns or of composite yarns containing both artificial silk and other textile fibres.

With the consent of the Author, the Translator has added a short chapter on the cellulose acetate branch of the industry, the developments in which appear to call for notice.

It is hoped, as was mentioned in the First Edition, that the practical information contained in this book will be of use to the scientific investigator as well as to those engaged in various branches of the textile industry.

THOMAS WOODHOUSE.

TRANSLATOR'S PREFACE TO FIRST EDITION

THE present volume includes practically all that appeared in the Second Edition of the French work, and also a considerable amount of information and new drawings concerning improvements which have taken place in the industry since the date of the publication of the French work. This addition has been supplied, and the original subject-matter suitably modified, by Mr. Foltzer, who has had much experience in the development of the Artificial Silk Industry.

The manufacture (spinning or drawing) of artificial silk yarns is explained and illustrated very fully ; but, in order to make the book more complete, the Author has written some very interesting pages on the production of artificial ribbon, lace, cloth, leather, and the like.

Altogether the treatise is very complete, and should form an interesting and valuable study, not only for those who are connected with the textile industry, but also for research students and others in the chemical and physical laboratories of our Universities and Technical Colleges.

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CHAPTER I

Introductory

NATURAL silk is, as is well known, the product of the silk-worm, which, when undergoing its metamorphosis from the caterpillar to the chrysalis stage, spins around itself a cocoon of silk. The organ which secretes the silk is composed of two openings situated at the mouth of the caterpillar. When the caterpillar is ready to spin its cocoon, this organ is full of a viscous liquid, similar in appearance to gum ; this liquid flows through the glands, and is drawn out to a thread of extraordinary length, and hardens on contact with the air.

Artificial silk has, in common with natural silk, only certain physical properties ; it is therefore only an imitation and not a substitute for the latter article. Moreover, no substance could be regarded as a substitute for natural silk without being proved and established as such by chemical means.

Artificial silk in the form of yarn is simply cellulose transformed into fine threads. Although several attempts have been made to manufacture artificial silk from other substances, it has been proved that cellulose is the best material for the purpose, since it occurs in large quantities, and can be obtained at a comparatively low price.

CHAPTER II

Cellulose : The Mercerizing of Vegetable Fibres and Fabrics

CELLULOSE.—Cellulose, which is the principal constituent of the tissues of plants, is, according to Cross and Bevan, the structural basis of the vegetable world. It is found in the natural state in all vegetable matter, and under many different forms, but not as a pure substance ; it is invariably in combination with other substances. The molecular constitution of cellulose is still almost unknown, but its empirical composition corresponds to the formula $(C_6H_{10}O_5)n$.

The principal vegetable tissues, after the exhaustive action of neutral solvents, form an organic body composed of the following substances—

(1) The various forms of cellulose (cellulose, paracellulose metacellulose).

(2) Vasculose.

(3) Cutose.

(4) Pectose.

(5) Calcium pectate.

(6) Nitrogenous substances.

(7) Various mineral substances.

The name cellulose is given to the substance which constitutes essentially the framework of vegetables, and even, according to Payen, Loewig and Kolliker, that of a certain number of the lower order of animals. It derives its name from the fact that it has ordinarily a cell-like structure. We shall leave aside animal cellulose, and shall deal here only with vegetable cellulose.

Vegetable Cellulose.—In the natural state cellulose is found in all vegetable matter, but under very different forms. In alcoholic fermentation the *Saccharomyces cerevisiae* which produces this reaction, and which constitutes yeast, is transformed in some degree to cellulose. Lichens, seaweeds, young organs of plants, contain cellulose under a form that permits

of its being readily isolated ; it is found with a more compact texture in the pith of trees, vegetable hairs, textile fibres, the succulent or fleshy parts of fruit, rootlets, and rapidly growing roots.   The cellulose of wood and of fruit stones, on the contrary, is encrusted with substances that sometimes give to it the property of extreme hardness.   On the other hand, cellulose is often found in an almost pure state in old linen, certain cottons, in white and rice papers.   According to M. Fremy, the framework of vegetable matter contains the following substances :   *True cellulose* or pure cellulose, soluble in Schweitzer's reagent (ammoniacal solution of copper oxide) ; *paracellulose,* soluble in this reagent after treatment with acids ; and *vasculose,* which is insoluble.   The action of Schweitzer's reagent on cellulose was first observed by Mercer, who used a solution of ammonia of 0·920 specific gravity, saturated with hydrated oxide of copper, then diluted with three times its volume of water.   He also showed by this treatment that the solution of cellulose is retarded by the presence of salts, and that in consequence solutions obtained by decomposing the copper salts by an excess of ammonia are much less active than solutions of equivalent strength which contain only the hydroxide.   Mercer showed in addition that an elevation of temperature retarded the activity of the solution, which action became very feeble at 35° C. (95°F.).   This question of temperature was therefore well known before the time of Pauly's patent (December, 1897).

Vasculose, or, according to Fremy, the third elementary constituent of vegetable matter, constitutes the skeleton or framework of vegetable cells.   It contains more carbon and less hydrogen than cellulose ; it unites the cells and the fibres. It is sometimes found in the interior of the tissues in the form of a horny membrane.   It constitutes the heavy part of vegetable matter, is insoluble in a mixture of one part of sulphuric acid and two parts of water, and also in Schweitzer's reagent.   It does not dissolve under ordinary pressure in alkaline solutions, but it dissolves under a certain pressure. Vasculose dissolves in solutions of oxidizing agents, such as chlorine water, hypochlorites, nitric acid, chromic acid, permanganates, etc. ; before dissolving, it changes into a resinous acid which is soluble in alkalies.

To separate vasculose from cellulose, M. Fremy used the above-mentioned mixture of one part of sulphuric acid and

two parts of water, which dissolved only the cellulose ;
Schweitzer's reagent acts in the same way. If it is desired to
dissolve the vasculose so that the cellulose may be directly
acted upon, the organic tissue must be left for several hours
in contact with nitric acid diluted with its own volume of
water. This transforms the vasculose into a yellow resinous,
acid soluble in alkalies. The cellulose is then obtained by
adding an alkaline solution which dissolves the yellow acid
and leaves the cellulose unaltered.

The transparent membrane situated on the outer surface
of vegetable matter is known as cutose.

The suberin is formed by the union of cutose and vasculose.
Cutose also resists the action of the above-mentioned mixture
of sulphuric acid and water, but it dissolves in dilute solutions
of potassium or sodium carbonates. With nitric acid it
produces suberic acid. To separate cutose, use is first made
of Schweitzer's reagent, then of the potash, employed a second
time without pressure. The first reagent (H_2SO_4 and H_2O)
attacks the cellulose, the second attacks the cutose, and the
last dissolves the vasculose.

Pectose is insoluble in water, but it becomes soluble and is
transformed into pectin by the action of dilute acids. Pectose
is dissolved by the action of warm dilute hydrochloric acid on
organic tissues, and the pectin thus formed dissolves in the
water and is precipitated with alcohol.

Pectate of lime is the basis of the membranous tissue that
binds the cells together, for in the decomposition by acid s the
tissue is disintegrated. The tissue is treated in the cold with
dilute hydrochloric acid ; this dissolves the lime, and leaves
the pectic acid as an insoluble residue. This residue is treated
with a dilute solution of potash, forming a soluble pectate
which can be decomposed by acids. The nitrogenous, and
inorganic substances are treated according to the ordinary
methods. Nitrogenous substances are dissolved in alkalies,
and inorganic substances are found in the ash after calcination.
Wood contains, in addition, 4 per cent. xylon or incrusting
substances.

Properties.—Cellulose is a ternary compound which may
be considered as a polyglucoside formed by the condensation
of at least two molecules of $C_6H_{12}O_6$. The formula for cellulose
is $(C_6H_{10}O_5)n$, and its percentage composition is shown in the
following table.

—	$C_6H_{10}O_5$.	Wood.	Cotton.	Linen.	Paper.
Carbon	44·44	43·87	43·30	43·63	43·87
Hydrogen	6·14	6·23	6·40	6·21	6·12
Oxygen	49·42	49·40	50·30	50·16	50·01
	100·00	100·00	100·00	100·00	100·00

—that is to say, in terms of carbon and water, the percentages for wood may be expressed as under—

Carbon	43·87
Water	56·13
	100·00

In the pure state cellulose is a white, transparent solid, without smell or taste. It is insoluble in cold water, alcohol, ether, fatty or volatile oils. Its specific gravity varies from 1·25 to 1·45. When heated to a temperature of 200° C. (392° F.), it decomposes into water, acetic acid, pyrocatechin, complex empyreumatic products, and carbon, which retains in general the form of the original body. When cellulose is pure it is unaffected by exposure to air ; but wood cellulose is decomposed owing to the presence of substances containing nitrogen ; this is what takes place during the rotting of vegetables.

Hygroscopic Moisture.—All air-dried vegetable tissues retain a certain quantity of water which is liberated at a temperature of 100° C. (212° F.), but on being exposed to the air under ordinary conditions the material again attracts moisture and regains its original condition. The amount of water thus absorbed varies from 6 to 12 per cent. in the different celluloses. This property of attracting moisture is a property of cellulose itself, and depends upon the presence in the molecule of OH groups, for it has been observed that the property of attracting moisture decreases with the suppression of these hydroxyl groups. The quantity of moisture that the celluloses absorb in an atmosphere saturated with water vapour is necessarily much greater than that absorbed in the ordinary atmosphere.[1] Similarly, all fibrous or amorphous modifications of cellulose have the property of attracting hygroscopic

[1] H. Müller, *Pflanzenfaser.*

moisture ; this property does not depend upon the form of the celluloses—it is a physical or chemical phenomenon.

Vegetable celluloses lose water as they, mature, and during their growth the plants contain hydrated modifications of cellulose which are converted into less active forms by simple dehydration. Cotton is one of the least active forms of cellulose, it being known that pure or fully bleached cotton enters into reaction with acids, alkalies, or oxides only under special conditions.

Concentrated ammonia has no action on cellulose even at 100° C. (212° F.). At 200° C. (392° F.), however, combination
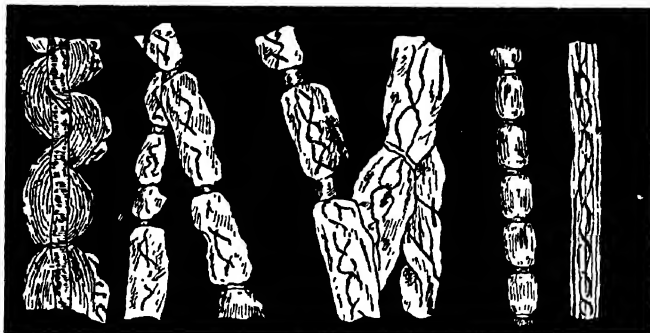
takes place, and the presence of NH_2 in the cellulose is proved by the affinity of the latter for basic colouring matters.[1]

Cellulose is soluble in copper hydroxide dissolved in ammonia (Schweitzer's reagent). When cotton fibres are immersed in this solution they shrink from 40 to 60 per cent., then swell out to about six times their original diameter, decompose, and finally dissolve. The appearance of the cotton fibres, previous to decomposition and solution, is shown on an enlarged scale in Fig. 1 (Hoehnel and Kittredge). If the solution of cellulose is Schweitzer's reagent is neutralized with a slight excess of HCl, the cellulose is precipitated in flocculent form without having undergone any modification. Cellulose is insoluble in weak alkalies, in alkaline carbonates, and in chlorine water. On this last property depends the art of bleaching cotton, hemp, or linen fibres with hypochlorites, but it must be

[1] *Mon. Scient.*, p 1. 1970).

remembered that the threads or tissues are attacked and weakened if they remain too long in contact with the bleaching agent.

Action of Alkalies.—Cotton cellulose is practically unaffected by dilute alkaline solutions even at high temperatures. Thus a solution of caustic soda with 1 to 2 per cent. Na_2O has no apparent action, even at temperatures of 100° C. (212° F.), and higher. Advantage is taken of this feeble action in the textile industry, for it has, as a direct result, the closer binding of the tissues, and, in addition, gives them the property of absorbing colouring matters more readily, and thus yielding deeper shades. The action of milk of lime is avoided because it has an injurious effect upon the fibres. Concentrated alkaline solutions, on the contrary, have, even in the cold, a remarkable effect on cellulose, and modify completely its molecular constitution. The cotton fibre, which has a form more or less like a tube flattened longitudinally, changes its shape completely when treated with these solutions ; the fibre swells out into cylindrical form, and the large central canal is considerably reduced in size. The fibre shrinks considerably in the length and becomes translucent. These results are due to a definite reaction between the cellulose and the alkaline hydroxides, which is accompanied by combination with water. The cellulose emerges from this treatment as a form of hydrate, the action being termed " mercerizing."

Mercerization or Mercerizing.—It was in the year 1844 that John Mercer, a Lancashire calico printer, commenced his researches relative to the action of caustic alkalies on textile fibres. As in a number of cases, an element of chance entered into Mercer's discovery. In the course of a study on the phenomena of capillarity produced by various liquids, he observed, after filtering concentrated caustic-soda solution through a cotton fabric, that the latter had undergone characteristic modifications. A contraction had taken place both in the length and in the breadth of the fabric, and the fibre, which had become thicker, had acquired a certain amount of transparency. At the same time the specific gravity of the filtered caustic-soda solution had diminished from 1·3 to about 1·265 ; this led him to think that a part of the alkali had combined chemically with the cellulose. This preliminary observation induced Mercer to pursue the study of this action on cotton, to which he himself gave the name of mercerization.

He obtained the best results in operating, both with bleached fabrics and with scoured fabrics, below the boiling point with a lye of caustic soda. The cloth was placed into the caustic soda solution registering from 26° to 29° Bé. at a temperature of 15° C. (59° F.).

After removing the soda by a thorough washing, the mercerized cotton assumed quite a different appearance. The fibre was thicker, more regular, and more transparent ; instead of having the appearance of a flattened ribbon or tube with thickened edges, and the characteristic twist of cotton, it swelled out and gained in thickness, partly at the expense of the central canal. The latter, which formerly traversed the whole length of the fibre, had now almost completely disappeared.

From the beginning Mercer had established the fact that the threads shrank from 20 to 25 per cent. of their original length. A cloth which counted 200 threads to the square inch contained 270 threads per square inch after having been mercerized. The resistance to breaking had increased at the same time, the increase being not less than 69 per cent. in the case of cloths, and 46 per cent. for threads.

The mercerized cloth had gained from 4·5 to 5·5 per cent. in weight, and this increase was due to its combination with water. This water was liberated when the cloth was heated to 100° C. (212° F.), but an equivalent amount entered again into combination on exposing the fabric to the air. Mercer admitted that the cellulose formed with the soda a combination with the formula $C_{12}H_{20}O_{10}.Na_2O$, which, after washing, was transformed into $C_{12}H_{20}O_{10}.H_2O$. These formulae are based on the increase of weight which the fibre acquires when treated with an alkaline solution and then thoroughly washed.

We might mention here that Cross and Bevan have applied the name of " hydrates " to those modifications of cellulose which contain " water of hydration " in addition to hygroscopic moisture. As already mentioned, the latter is dependent on atmospheric conditions, and may be expelled by heating to the boiling point of water ; but, on the other hand, " water of hydration " depends upon the constitutional modification, and it is more firmly held than ordinary hydroscopic moisture. For mercerized cotton they have given the formula $(C_6H_{10}O_5)_2.H_2O$, and for cellulose regenerated from viscose the formula $(C_6H_{10}O_5)_4.H_2O$.

The amount of contraction which takes place in cotton threads mercerized without tension has been accurately determined in the following manner : A certain number of cotton hanks of the same count and of the same twist were immersed in soda lye (12 and 20 per cent) with and without the addition of salt. The hanks were then washed to remove the soda, and afterwards dried and remeasured.

With 12% soda and without salt, the contraction was 11·5 per 100
„   12%   „   with   „   „   6·8 „ 100
„   20%   „   without „   „   18·6 „ 100
„   20%   „   with   „   „   15·7 „ 100

The contraction is therefore much less when the soda is saturated with salt.

The formula which is given to the mercerized cellulose is the same as that which Aimé Girard has assigned to hydrocellulose, a substance which he obtained by the action of concentrated sulphuric acid as cellulose (1881). The fact that cellulose, mercerized with caustic soda, and hydrocellulose are practically the same substance should not create any surprise, since it was shown by Mercer that concentrated sulphuric acid (as well as zinc chloride) had practically the same effect on cotton as soda.

Besides the properties that are mentioned above, mercerized cotton acquires the remarkable property of having in general a greater affinity for colouring matters than the original cloth. These colouring matters are more easily fixed in the mercerized fibres or cloth, and the colours imparted are deeper and more lustrous. In addition to these advantages, the process of mercerizing effects economy in the use of colouring matters.

A very interesting document from an historical point of view is found in the work of Kurrer, *Druck und Farbekunst*, which appeared in 1859. This article discusses Mercer's discovery and the possibility of its application.

We may here draw attention to a demonstration by Mercer which consisted of the application of a solution of copper nitrate on certain parts of the surface of a cotton fabric. These parts were afterwards treated with a weak solution of caustic soda in order to decompose the nitrate. After washing, to remove the alkali, and partial drying in air at the ordinary temperature, he exposed the fabric to ammonia vapour, and

One interesting feature is that the cause of the brilliancy of cotton mercerized under tension is the same as that of artificial silks, and depends only on the geometrical properties of the fibre.

Although imitation silk, made by mercerization of cotton, does not attain the incomparable brilliancy of artificial silk, it is superior in respect to strength and resistance to breaking. The lack of strength is the chief defect of artificial silk ; and most types of artificial silk are weakest when wet.
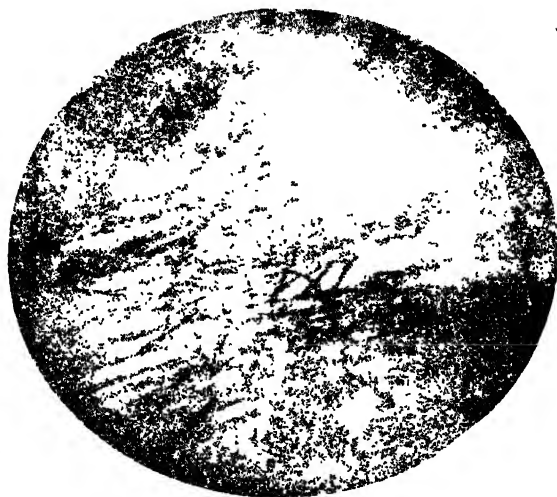
FIG. 2.

Figs. 2, 3, 4 and 5 are photo-microscopical views of cotton fibres in different stages. Fig 2 is an enlarged view of a number of cotton fibres. Fig. 3 shows mercerized cotton which has just been immersed in a solution of copper oxide in ammonia. Fig. 4 illustrates mercerized cotton partially dissolved in ammoniacal copper-oxide solution (the undissolved parts are shown by the white patches near the middle of the illustration) ; and Fig. 5 shows the complete solution of the cotton fibres ready to be filtered before being transformed into threads of artificial silk.

Action of Acids.—The action of acids on cellulose is very important. Sulphuric acid varies greatly in its action according to the degree of concentration. If pure cellulose, in the

form of unstarched white paper, is immersed in a mixture of two volumes of acid and one volume of water, and allowed to remain in contact only for about thirty minutes, the appearance of the substance is entirely changed. The acid is removed by washing, first with ammonium hydroxide, and then with distilled water. The paper, under this treatment, has become stronger, translucent, slimy to the touch ; it will no longer filter, but it is useful in experiments in dialysis, and has been employed in the osmosis of sugar, because it
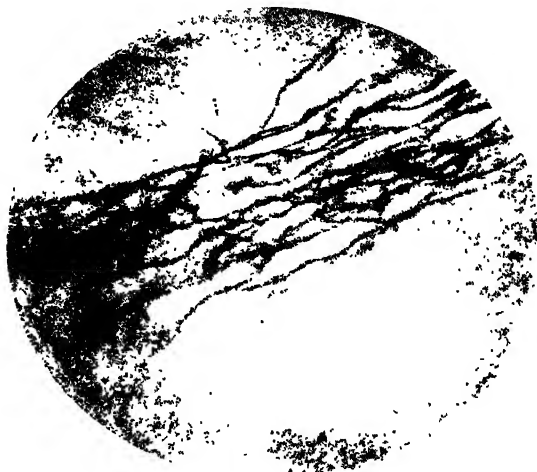
FIG. 3.

will allow liquids to mix or diffuse with each other through its pores. The paper has been transformed into the substance which Messrs. Ponmarede and Figuier discovered in 1846, and to which they gave the name of vegetable parchment. The manufacture of this parchment paper was commenced in England in 1857. If it is desired to make careful observations on this reaction, the sheet of paper must be weighed before treatment to determine its humidity and to estimate the cellulose during the process. For this estimation it is necessary to treat the acid and the water that have been used for washing.

If the cellulose has been left too long in contact with the sulphuric acid, the parchment paper is disintegrated, and is converted, without undergoing any change of colour, into a

soluble cellulose which has no rotatory power, whereas that of soluble starch has a rotatory power of $+\cdot211°$. The substance is then converted into a special dextrine, which is coloured blue by iodine, as are all starchy substances ; this dextrine is dextrorotatory, but not so much so as starch. The coloration of cellulose by iodine in presence of sulphuric acid has been employed in micrography, since the time when Cramer made his observations, to detect the presence of this substance.

Fig. 4.

If the action of the sulphuric acid on cellulose is allowed to continue, the dextrine is transformed into two glucoses, especially when it is subjected to prolonged boiling. If the action of the acid is very much prolonged, it leads to the production of ulmic compounds, such as ulmin $C_{48}H_{28}O_{14}$, and of compounds analogous to peat, lignite, oils and anthracite ; but if manganese dioxide be added to the product, the resulting substance is formic acid.

Several years ago a new industry was established to deal with the action of sulphuric acid on fine cotton yarns, an industry that has developed considerably, especially in Switzerland. It was known that sulphuric acid, of concentration between 50° and 60° Bé., had a mercerizing effect on cotton. An important factory has been erected at Wattwil,

Switzerland, where, within the last few years, a new and beautiful product has been made by apparatus described in the patent specifications of la Soc. Ame. Heberlein & Cie. By these processes, a very fine muslin fabric can be passed rapidly between two or more cylinders in a sulphuric acid bath of the above-mentioned concentration.   The fabric is completely transformed and an effect imparted to it which rivals the brilliance of silk.   It is not a process of mercerization,

Fig. 5.

however, that produces the effect, but the action of an acid which partially dissolves the outer surface of the cotton fibres or yarns, and changes these parts into a fibrous or colloidal mass, as compact and brilliant as artificial silk.   The resulting effect is due jointly to the degree of concentration of the acid and the speed of the cloth.   If, for example, a muslin fabric be left for two minutes in the sulphuric acid bath, it becomes uneven and totally ruined ; whereas, if the fabric be passed quickly through the acid, and then immediately through water, the threads of the fabric are attacked only for a short time, their surfaces, as indicated, are partially dissolved, and then reprecipitated by the immediate treatment with water ;   the resulting product is brilliant and transparent. As a matter of fact, fabrics thus treated are known as " Transparent Textiles," and have a moiré effect.

The machines and installations for producing these trans-
parent textiles are, on the whole, very simple. The fine
muslin fabric is first bleached and dried as in the case of
ordinary fine cotton cloth. Then it is wound on a roller and
subjected to a light tension while passing through a sulphuric
acid bath of 50° to 60° Bé. concentration, and at a speed
somewhat similar to that employed for mercerization. A
common concentration of the acid is 53° Bé., and the fabric is
run through this liquid at 10 metres (approx. 11 yards) per
minute. The surplus acid is then pressed out by ebonite
cylinders, and the cloth immediately led into a bath of water
which is renewed continuously. The treated fabric is after-
wards well washed to remove all traces of acid, then mercerized
with soda and dried.

Instead of mercerizing the fabric after the acid treatment,
it may be mercerized after bleaching and, of course, before
passing it through the acid bath. This mercerization, early or
late, is absolutely necessary to obtain great brilliance and
perfect transparency. The treated fabric is finally dried
under great tension by means of special apparatus. A great
difficulty is experienced in the final drying, for the effect of the
acid causes the threads and picks of the cloth to adhere to each
other. The starchy defect, if not displaced, would leave
the fabric hard and practically useless ; the defect is removed
by specially constructed stentering machines.

Messrs. Heberlein of Wattwil have spared no effort to bring
their methods to perfection, and are now able to obtain
multiple and diversified effects on transparent textures.
If, for example, before passing the bleached cloth through
the acid bath, it is passed through a printing machine, and
then a kind of varnish or a type of greasy soap applied to the
decorative ornament to act as a resist, the parts so treated are
not affected by the transparency treatment which follows.
After passing the prepared fabric through acid and water
baths, all the ground part of the cloth would be rendered
transparent, while the figured portion would be more or less
opaque. The resists are afterwards removed by washing
in warm water. Fabrics thus treated, and afterwards dyed,
are of special beauty, seeing that different shades of colour
appear on the transparent and opaque parts.

The industry engaged with the production of transparent
textiles is already a very important one, and is possible of

great expansion, since other firms have searched and found different processes involving the use of sulphuric acid as base, and other products have been obtained by rapid dissolving actions.

Nitric acid modifies cellulose in a very remarkable manner. When the fuming acid is employed, a very energetic action is produced even in the cold—the substance obtained explodes if it is heated to 120° C. (248° F.), or if it comes in contact with a light. This is pyroxylin, or guncotton. Bracconot pointed out this modification as early as 1833, but in 1847 Schœnlein showed that in order to obtain a good product it was preferable to soak the cotton or the cellulose in a mixture of three parts of concentrated nitric acid and five parts of sulphuric acid. After having been in contact for about an hour the combination is complete.

$$C_{24}H_{40}O_{20} + 5(HNO_3) = 5(H_2O) + C_{24}H_{35}O_{20} \cdot 5(NO_2)$$

Cellulose.　　Nitric Acid.　　　Water.　　Pyroxylin.
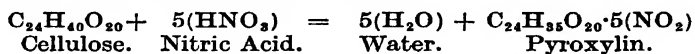
When cellulose is brought into contact with nitric acid at a low temperature a nitrated derivative is formed ; the degree of nitration depends upon the concentration of the acid, upon the duration of contact, and upon the physical state of the cellulose itself. According to Béchamp there are several kinds of nitrated celluloses, for cellulose loses successively a number of molecules of water that are replaced by an equal number of molecules of nitric acid. The product has a similar appearance to the substance from which it has been prepared, and has almost the same consistency ; it is, indeed, a little harder to the touch than ordinary cotton, and there is an increase in weight, since 100 parts of cotton yield 175 parts of pyroxyle.

The formulae are as follows—

Tri-nitro-cellulose　　.　　.　　.　　$C_{24}H_{37}O_{20}.3(NO_2)$.
Tetra-nitro-cellulose　　　.　　.　　$C_{24}H_{36}O_{20}.4(NO_2)$.
Penta-nitro-cellose or pyroxyle　.　　$C_{24}H_{35}O_{20}.5(NO_2)$.

If cellulose be represented by $C_{24}H_{40}O_{20}$, the nitro-celluloses are $C_{24}H_{40-x}O_{20}.(NO_2)_x$.

These compounds, when burning, liberate an enormous volume of gas (carbon dioxide, carbon monoxide, nitrogen and water vapour). In consequence of this property attempts have been made to replace the powder used in firearms by guncotton. The substance has been discarded, however, because its action is too violent.

When, say, 55 grms. of carded cotton are immersed in a mixture of 1000 grms. concentrated sulphuric acid and 500 grms. nitric acid (specific gravity 1·367), or in a mixture of potassium nitrate and hydrated sulphuric acid in the proportion of 8 to 12, a special guncotton is obtained (that is to say, the octo-nitro-cellulose, $C_{24}H_{32}O_{12}.8(NO_2)$ of Maynard) after having been washed with a large quantity of water, freed from traces of acid, and then dried in the air. This substance, insoluble in alcohol and in ether, dissolves in one part of alcohol and three parts of ether, and thus gives the product known as collodion, which is used in photography and in medicine. It is also used in commerce under the name of artificial leather, for M. S. Robe has brought forward a product which is simply collodion in comparatively thick sheets which have been soaked for some seconds in sulphuric acid diluted with its own volume of water. This new substance can be tanned and coloured very easily. Collodion combined with camphor is ultimately transformed into celluloid. [1]

The mono-hydrated organic acids, such as stearic, butyric and benzoic acids, form, with cellulose, neutral compounds analogous to the glucosides (Berthelot).

Boiling concentrated acetic acid does not disintegrate cellulose, but at a temperature of 190° C. (374° F.), in a closed vessel, the mixture forms a yellowish liquid product, from which water precipitates white flakes of acetic cellulose.

$$C_{24}H_{37}(C_4H_3O_2)_3.O_{20} \text{ (Schlossberger).}$$
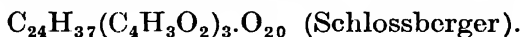
[1] Celluloid is a solid homogeneous body ; it is transparent, colourless, or slightly inclined to a yellowish tint ; odourless when sufficiently dry ; tasteless ; specific gravity, 1·37 ; a feeble odour of camphor is emitted if heated or subjected to friction. It is a very bad conductor of heat and of electricity, and its elasticity is comparable to that of ivory. It is very ductile and very malleable when hot.

Its manufacture : As has already been stated, this interesting substance has cellulose for its basis, whence it derives its name. Its preparation involves six distinct stages—

1. The transformation of cellulose into pyroxylin.

2. The pounding and subsequent bleaching of this pyroxylin, and its partial drying.

3. The crushing or pulverizing of the bleached material, and the addition of camphor soaked in alcohol.

4. The transformation of this mixture of bleached cellulose, camphor, and alcohol into a kind of collodion.

5. The solidification of the collodion into a homogeneous substance.

6. The spreading and the drying of the formed masses.

It has been found that mercerized cellulose acetylates more slowly than unmercerized cellulose ; the former is not even attacked at boiling point if the operation is carried out without sulphuric acid.

Cellulose is immediately charred by boron fluoride, BoF_3 ; zinc chloride does not attack it.   The latter fact is interesting, for it affords a means of distinguishing between vegetable and certain animal fibres.   Thus, in a neutral solution of the salt, raised to a temperature of 60° C. (140° F.), silk is easily dissolved, whereas linen, hemp and cotton are unaffected. The action is similar to that obtained with the ammoniacal solution of nickel oxide (Schlossberger).

Preparation.—To obtain pure cellulose it is usual to employ cotton, paper, pith of trees, etc.   These materials are submitted successively to water, caustic-soda solutions, and hydrochloric acid ; washed with alcohol, ether and water, and then dried.   The product is recovered with boiling glacial acetic acid and boiling water, and the substance is finally dried at a temperature of 100° C. (212° F.).

CHAPTER III

Origin of Artificial Silk

ORIGIN OF ARTIFICIAL SILK.—The idea of producing artificial silk is not by any means a modern one. Réaumur, the French physicist and naturalist, indicated the possibility of its manufacture in 1754. In his memoirs relating to the history of insects he states explicity : " Silk is only a liquid gum which has been dried ; could we not make silk ourselves with gums and resins ? This idea, that would appear at first sight fanciful, is more promising when examined more closely. It has already been proved that it is possible to make varnishes which possess the essential qualities of silk. China and similar varnishes are unaffected by solvents ; water has no effect on them ; the greatest degrees of heat to which our fabrics are exposed could not change them. If we had threads of varnish we could make them into fabrics which, by their brilliancy and strength, would imitate those of silk, and which would equal them in value, for good varnishes when properly dried have no smell. But how can we draw out these varnishes into threads ? We cannot, perhaps, hope to draw out these threads as fine as those obtained from silkworms, but this degree of fineness is unnecessary, and it does not seem impossible either to spin them into threads, or to spin them even as fine as natural silk, when we consider to what extent art may be carried."

It was, however, only after the discovery of nitro-cellulose and the properties of this substance that attempts were made with the idea of the production of threads which would approach in appearance those of natural silk. In 1855 Audemars of Lausanne took out a patent for transforming dissolved nitro-cellulose into fine threads which he termed artificial silk. At a later date this idea was worked out practically by transforming a solution of cellulose into an artificial thread which was employed as a conducting filament in electric globes.

But from a textile point of view these attempts were not crowned with success ; and it was only after numerous

experiments by Count Hilaire de Chardonnet, the great pioneer of artificial silk-making (1886), that the products of this manufacture became an article of commerce. However, before M. De Chardonnet it is only right to mention the names of Swan, Wynne, Powell, Swinburne, and Crookes, all of whom contributed to the great invention of the manufacture of artificial silk.

The different varieties of artificial silk employed in commerce are simply pure cellulose that has acquired the lustre of natural silk. They are distinguished, therefore, from the product of the silkworm by not containing nitrogen. All artificial silks have some form of vegetable fibre for their origin ; sometimes in the form of cotton, and sometimes as wood pulp.

There are five different methods which are employed, or probably will be employed some day, for the manufacture of artificial silk. In each of these methods a different solution is used. Thus—

(1) The artificial silk of Chardonnet, made from nitrocellulose.

(2) The Despeissis artificial silk, formed from a solution of cellulose in ammoniacal copper oxide, and known as the cuprammonium process.

(3) Viscose, or artificial silk made from thiocarbonate of cellulose.

(4) The lustrous artificial silk made from a solution of cellulose in zinc chloride.

(5) Acetate silk or " Celanese " made from acetic anhydride.

CHAPTER IV

Chardonnet Artificial Silk

(Nitrocellulose Process)

THE ARTIFICIAL SILK OF THE COUNT DE CHARDONNET.—The processes of Chardonnet have been described in a number of reports and technical reviews, so that we need give here only a summary description of them. The product of this manu-. facture first came into prominence at the Paris Exhibition in 1889. From that time the processes of Chardonnet have been carried on in several works in France and in other countries— in France at Les Établissements de Chardonnet à Besançon ; in Germany at La Société des fabriques réunies de soie artificielle à Frankfort ; in Switzerland at L'Usine de Spreitenbach, canton d'Argovie ; in Belgium at Les Fabriques de Tubize et d'Obourg. From time to time the methods of Chardonnet have been modified, with the result that the modern article is a very valuable product.

Nearly twenty years ago M. Ch. Schaublin, a teacher of chemistry in Basle, obtained the nitro-cellulose of gun-cotton by treating, as we have already pointed out, pure cellulose with a mixture of potassium nitrate and sulphuric acid. The solution of this product in ether and alcohol yields the well-known collodion, which, when in contact with air, forms a compact and elastic substance.

The Old Process.—Originally cellulose (cotton, straw, wood, etc.) was transformed into gun-cotton, and the latter dissolved in alcohol and ether ; collodion was thus obtained, as has already been mentioned. To this product was added perchloride of iron, or chloride of zinc and tannin. This substance was drawn out in the form of a thread which was passed through water acidulated with nitric acid. The thread was afterwards treated in the same way as natural silk. Dyed silk was obtained by adding suitable colouring matters to the collodion.

The Modern Process.—The method that is now practised is much more complicated than the older method, but it has the distinct advantage of producing a thread of superior, quality. Here the raw material is washed cotton. Its transformation into nitro-cellulose (gun-cotton) is accomplished by

immersing 4 kgs. (8·816 lbs.) of cotton in 35 litres (7·7 gals.) of a mixture of nitric acid and sulphuric acid ; the proportions being 15 per cent. of nitric acid, specific gravity 1·52, and 85 per cent. of ordinary sulphuric acid. The cotton remains in the mixture from four to six hours, and the degree of nitration depends upon the time of immersion. This degree of nitration can only be determined with a microscope and by the aid of polarized light. The acid is afterwards pressed out of the nitro-cellulose, and the latter is then washed until no trace of acid remains. Finally, the water is removed from the substance by means of hydraulic presses or hydro-extractors until there remains not more than 36 per cent. of water. In this state the nitro-cellulose is inflammable only to a slight degree, a condition which is of great importance for its ultimate use. To 22 kgs. (48·488 lbs.) of this nitro-cellulose are added 100 litres (22 gals.) of a mixture of equal quantities of ether and alcohol. This solution is then filtered and kept in large reservoirs. Experience has shown that a solution which has been kept for several days will produce a better quality of silk than a freshly prepared solution. From this pulp the silk is afterwards spun. For this purpose a very simple apparatus is used, consisting of a certain number of glass tubes, each drawn out to a capillary tube or spinneret with a bore varying from 0·1 mm. to 0·2 mm. The nitro-cellulose is forced through these capillary tubes under a pressure of 60 kgs. per square centimetre (853 lbs. per sq. in.). Several of these threads are grouped together as they pass through a guide to be wound untwisted on to a bobbin ; the group corresponding in count to one thread of natural silk. On drying, these threads acquire a certain degree of lustre, strength and elasticity. The threads are dried in a stove which is heated to 45° C. (113° F.), and which is well ventilated. In this manner the alcohol and the ether still present in the silk are volatilized, and, in consequence, the degree of inflammability of the thread is lowered considerably. However, in order to render the thread absolutely non-inflammable, it should be denitrated—an operation which is carried out in a bath of alkaline sulphides. Thus a thread is produced which possesses strength and elasticity ; its colour is inclined to yellow, but the thread may afterwards be bleached with chloride of lime. Artificial silk is now dyed in much the same way as natural silk, basic colouring matters being used, and

no longer by adding colouring matters to the nitro-cellulose, as was recommended in the first process.

At a conference on artificial silk made from nitro-cellulose, which was held at l'Institut Chimique de Nancy, Mr. K. Haller, a teacher of organic chemistry at Sorbonne, stated that the Count de Chardonnet, after having tried several varieties of cellulose, fixed upon cotton and wood pulp, which he nitrated under special conditions. He attached, moreover, very great importance to the following points—

(1) Perfect drying of the cellulose. This drying takes place in stoves, which, for preference, should be provided with gratings of copper or iron tubes, through which pass hot water or steam at a temperature of 90° to 100° C. (194° to 212° F.).

(2) Concentration of the acids. The concentration of the acids is of the highest importance, not only for the degree of nitration, but also for the subsequent solubility of the products.

(3) Washing of the partially dried products. This operation must be conducted without rise of temperature, and completed in a hydro-extractor of special construction in which the alternate processes of drying and wetting with pure water are repeated several times. After having completed these operations, the substance is often bleached by means of a small quantity of chloride of lime and nitric acid. The pyroxylin first obtained, after being properly washed and dried, is dissolved in a mixture of alcohol and ether in order to obtain collodion, of which 100 litres (22 gals.) contain—

Rectified ether at 65°	.	.	.	.	36 litres	(7·92 galls.)
Alcohol at 95°	.	.	.	.	64 ,,	(14·08 ,,)
Pyroxylin	.	.	.	.	5 kilogs.	(11·02 lbs.)

Afterwards, the discoverer showed that there are two kinds of tetranitro-pyroxylins—one anhydrous, which is obtained by complete drying, and which is that generally known and used ; while the second kind is hydrated, and contains from 16 to 20 per cent. of water of constitution ; it differs from the first by its optical properties (action on polarized light) and by its solubility. It is obtained by first washing well the cellulose which it is desired to nitrate, then pressing it without removing the whole of the water, so that when pressed it should contain 30 per cent. of its weight of water. This water being partly water of constitution and partly uncombined water, the solution obtained with this nitro-cellulose

in alcohol and ether is almost one-third more fluid than the solution of anhydrous pyroxylin. This solution, which is conducted or spun through special capillary tubes invented by M. De Chardonnet, need no longer pass through water to produce instantaneous solidification—the action of the air is sufficient ; consequently, spinning with the aid of water, as was seen carried on in the Paris Exhibition of 1889, has been replaced by a system of dry spinning, very similar to the old method, but in which the water jacket or tube and the current of water are dispensed with.

By the employment of hydrated pyroxylin, the operation of drying is dispensed with, and thus all danger of inflammability and of accident from explosion in the works is avoided.

Denitration.— The denitration of the nitrated cellulose, previously made up in the form of hanks, is always carried out in a solution of alkaline hydrosulphides. At Besançon, calcium hydrosulphide is employed, and is obtained from the works of Saint-Gobain à Saint-Fons, where it is made from the tank waste produced during the manufacture of caustic soda by the Leblanc process. Artificial silk buyers, as well as assurance companies, have compelled the manufacturers to perform the denitration thoroughly, and this in spite of several disadvantages that at first stood in the way. Consequently, since 1893 the silk, made by the Chardonnet process has become pure cellulose, and is similar in regard to combustibility to flax, hemp and cotton. Unfortunately, denitration removes part of the strength and elasticity of the thread, in addition to which the thread loses nearly two-thirds of its strength when wet. Nevertheless, the new thread was very quickly appreciated on account of its brilliance, which greatly surpasses that of natural silk.

In 1895 the price of artificial silk made by the Chardonnet process was 30 frs. per kilogramme (10s. 11d. per lb.) ; in 1896 it had fallen to 26·5 frs. per kilogramme (9s. 7½d. per lb.) ; in 1897 to 21·75 per kilogramme (7s. 11d. per lb.) ; and in 1898 it rose again to 25 frs. per kilogramme (9s. 1d. per lb.). At this time Europe had still little confidence in this new material, and practically all of it was exported into South America, where the same import duties were imposed as for natural silk.

Without speaking of the danger that arises from the preparation of collodion, we must mention that the drying

of this substance is a dangerous process, on account of its explosive nature.   Happily, Chardonnet discovered that nitro-cellulose, when only partially dried, dissolved in alcohol and ether as easily as dry nitro-cellulose did ; that the fluidity of pressed or partially dried nitro-cellulose or collodion was not inferior to that of dry nitro-cellulose, and that it spun equally. well in spite of the water which it contained.   These collodions can therefore be spun directly in the air, and the winding of the spun thread performed with a considerable speed ; also the mechanism of the machines used in the manufacture of these threads has, for these reasons, been very much simplified. The heavy vapours of ether must be removed from the work-shops by means of powerful aspirators.   None of the usual processes of denitration of cellulose (perchloride of iron, chloride of iron and alcohol, sulpho-carbonates, etc.) has been able to displace the alkaline hydrosulphides.

INTERESTING OBSERVATIONS ON THE STRENGTH AND ELASTICITY OF SILKS.[1]

Type of Silk.	Breaking Weight.	Elasticity (Percentages)
Nitro-cellulose spun by the Chardonnet process .	150	23
Ditto, after denitration and drying . . .	110	8
Ditto, after denitration, but undried . . .	25	—
Nitro-cellulose spun by the Bronnert process .	125	28
Ditto, after denitration and drying . . .	115	13
Ditto, after denitration, but undried . . .	32	—
Natural silk	300	18

REMARKS.—" Breaking weight " indicates the weight in grammes which the thread sustains at the moment when it breaks.

" Elasticity " indicates the percentage of extension at the moment of breaking.

The figures varied considerably according to the concentration of the solution, and to the care taken in denitration ; therefore those given must be considered as mean values obtained from a number of experiments. The figures correspond to a standard thread of 100 deniers.

The flexibility and lustre of the denitrated product vary greatly according to the nature of the hydrosulphide which is employed, and the conditions under which the denitration takes place.   Different hydrosulphides were used in different works, and as a result there was a lack of uniformity in the physical properties of the finished articles which led to com-plaints from the buyers.   With calcium hydrosulphide the

[1] See the *Journal of the Industrial Society of Mulhouse* for 1900.

thread becomes hard and brittle; its strength and its elasticity diminish greatly. Ammonium hydrosulphide denitrates successfully under the influence of heat, but care must be exercised in its use, and its application is expensive. Another disadvantage is its odour, which is very disagreeable, although it is less dangerous to health than that of concentrated sulphuric acid. Magnesium hydrosulphide has the advantage of being cheaper; it denitrates much more quickly, and it yields a stronger thread. A mixture of ammonium hydrosulphide and a salt of magnesium is more stable than pure ammonium hydrosulphide, and it does equally well for the purposes of denitration; its use, however, involves unnecessary expense.

By exercising certain precautions it is possible to denitrate with sodium hydrosulphide. In general it is best to denitrate at a low temperature. This precaution prevents the sulphur —which at the moment of reaction is liberated by the oxidation of hydrogen sulphide in presence of nitric acid—from being deposited on the fibre. For each hydrosulphide there is a limiting low temperature at which the denitration is rapidly performed; while at a still lower temperature the denitration is incomplete and proceeds slowly.

In practice it is necessary that the saponification of the cellulose ester of nitric acid should be accompanied by a complete reduction of the nitric acid produced. For complete reduction eight molecules of hydrogen sulphide would be required for one molecule of tetranitro-cellulose. By taking certain precautions, however, the denitration may be carried out with four molecules of hydrogen sulphide. The greater part of the nitric acid thus formed is reduced, and the resulting nitrous acid unites immediately with one of the bases present. Very little ammonia is formed. Ammonium sulphide produces, in small quantities, oxysulphide, sulphites and thiosulphates, which cause the sulphur to remain in solution in the form of polysulphides. In this manner the lustre of the fibre is not altered in the slightest by the presence of sulphur. The threads of the denitrated cellulose contain only traces of nitric groups. These groups are sufficient, however, for the identification, by means of diphenylamine, of artificial silks derived from cellulose by this process.

Messrs. Vivier,[1] Cadoret, Lehner and Gérard have endeavoured to produce imitations of Chardonnet's silk which,

[1] *Revue industrielle*, 1890 (p. 194).

however, would be free from the defects of the latter. All these inventions, however, have stopped at the experimental stage, and the samples that have been made lacked the lustre, the flexibility, and the homogeneity which are characteristic features of Chardonnet silk, and of that made by the cuprammonium process. It would thus appear that the addition to collodion of one or other of the great number of proposed substances results in the production of a thread which has lost more or less the above-mentioned qualities.

Lehner alone continued these experiments ; afterwards he equipped a manufactory in Switzerland, but he did not succeed in producing a salcable thread until he abandoned the use of all his patented substances, such as gum, resin, linseed oil treated with sulphur, etc., and employed only the pure nitrocellulose of Chardonnet. Some mechanical details constitute the difference between these two establishments.

In order to reduce the net cost of the silk, which was particularly high in France, Chardonnet concentrated his solutions so as to have pulp which, after drying, was only 20 per cent. of the original weight ; Lehner, on the other hand, spun concentrated collodion which was, after drying, only 10 per cent. of the original weight. Thus, the latter was able to adopt the original processes employed in the manufacture of filaments for electric globes—that is to say, he was able simply to cause the threads to pass through a water bath as they emerged from the capillary tubes.

For this process the air pressure on the closed reservoirs or tanks can be relatively diminished, so that it is possible to use glass stop-cocks connected by indiarubber tubing to the capillary tubes and to the pipes which convey the solution. Consequently, the openings of the capillary tubes can be made a little larger. On the other hand, it might be mentioned that the speed of winding the threads decreases with the pressure, which is a disadvantage.

Chardonnet, on the other hand, was obliged to use high pressures (60 kgs. per square centimetre and more, 853 lbs. per sq. in.) in order to be able to force his highly concentrated solutions through the openings of the capillary tubes. This pressure increases as the fluidity of the collodion diminishes, and the fluidity diminishes greatly for a slight increase in the concentration of the collodion.

The high pressure employed at Besançon is necessary,

partly for the high concentration, and partly for overcoming the friction caused by the passage of the solution through narrow openings. In consequence, the expenses are increased greatly ; strong pipes or conduits are necessary ; and the stop-cocks must be of superior construction in order to withstand successfully the high pressures. These disadvantages are compensated for only by the high speed attained in winding the threads.

Dr. Lehner noted that concentrated sulphuric acid and hydrochloric acid exercise a liquefying action on the collodion. Chardonnet observed that the addition to the collodion of aldehyde, ethyl-sulphuric acid, and ammonium chloride, also produced liquefaction. Unfortunately, the degree of fluidity obtained with all these substances is not great enough to merit their use in the highly concentrated solutions of De Chardonnet.

In 1895 Bronnert noted that alcoholic solutions of certain substances, whether organic or inorganic, dissolve tetranitro-cellulose easily (this fact had already been stated by Béchamp —see p. 17), whereas alcohol alone does not.

The degree of solubility, as well as the properties of the solution, varies according to the substances employed. According to Bronnert, calcium chloride would be the most satisfactory substance for obtaining solutions for use in the manufacture of silk. Pure water is used as a coagulating liquid. By evaporation of the solution on a glass plate a strong transparent elastic residue is obtained. Alcoholic solutions of ammonium acetate also dissolve tetranitro-cellulose very readily ; but the solutions obtained by this means have not the necessary viscosity for satisfactory spinning. When these solutions are raised to a high temperature in a vapour bath they become brown and acquire a degree of fluidity which renders them useless for the operation of spinning into thread. If they are evaporated on a glass plate, the residue possesses neither coherency nor elasticity, but crumbles on being touched.

Ammonium sulphocyanate dissolved in alcohol has also the property of dissolving tetranitro-cellulose ; but if this dissolved substance is allowed to remain for several weeks it turns into a gelatinous material of a yellowish colour.

The high degree of liquefaction produced by ammonium acetate is probably due to molecular change of the dissolved nitro-cellulose ; it is perhaps even a type of hydrolysis. An

exhaustive study of this reaction would perhaps enable con-
clusions to be drawn that would lead to the establishment
of the constitution of cellulose itself.   Finally, calcium chloride
seems to give a condensation product of tetranitro-cellulose
with alcohol.

It appears very reasonable, moreover, that the substance
known under the name of tetranitro-cellulose is an oxycellulose
ester.   In this case the nitration—that is to say, the esterifica-
tion—of four hydroxyl groups (OH) of the cellulose molecule
would be accompanied by oxidation, and part of the nitric
acid would be reduced to nitrous acid.   It would be interesting
to be able to establish by direct analysis the presence of the
ethoxyl group in the molecule of nitro-cellulose dissolved in
the solution of calcium chloride in alcohol.

Although solution is instantaneous when a molecule of
calcium chloride is added to a molecule of tetranitro-cellulose,
the maximum liquefaction is reached in about half an hour,
when the mixture is heated to 60° or 70° C. (140° or 158° F.)
and the vapour then cooled.

The fluidity of the solution can also be increased by nearly
30 per cent. if, before nitration, the cellulose be submitted
to an energetic hydration by mercerizing it, for example, with
caustic soda, and then washing it well with water.   The
nitration of cellulose can conveniently be followed by a slight
bleaching with lime ; the esterification of the four hydroxyl
groups (OH) seems to protect the molecule from subsequent
oxidation.   Chardonnet has shown that if the cellulose is
bleached with chlorine and then nitrated, the collodion,
manufactured from the nitro-cellulose thus formed, does not
spin so well as if the treatment with chlorine had been omitted.

It is evident that a great future awaits those manufacturers
who can produce an imitation of silk without the aid of nitro-
cellulose, which is dangerous and expensive, or of ether and
alcohol. [1]   The manufacturers of artificial silk who work with
ammoniacal solutions of copper, as well as those who employ
the " Viscose " and cellulose-acetate processes, may congratulate
themselves on having accomplished this.

[1] This condition has been achieved by the industrial application of
at least two other processes.—*Trans.*

CHAPTER V

Despeissis Artificial Silk
(Cuprammonium Process)

DESPEISSIS ARTIFICIAL SILK AND ITS MANUFACTURE (CUPRAMMONIUM PROCESS).—This silk, which is pure cellulose, is distinguished from artificial silk made from nitro-cellulose by its homogeneous composition. Like the silk of Chardonnet, it is remarkable for its lustre, strength and elasticity. The mechanical processes used are similar to those used for all artificial silk, its manufacture differing only in the chemical processes. The raw material is cotton, and the cellulose is dissolved in ammoniacal copper oxide. This solution is forced through capillary tubes of 0·18 to 0·2 mm. diameter into a mixture of sulphuric acid and water, and the threads thus formed are wound on to glass bobbins. These threads are afterwards washed in acetic acid or formic acid ; they are then dried, and wound on to bobbins, or reeled into hanks ready for sale.

The idea of producing artificial silk by this method dates from 1890, when a Frenchman, M. Despeissis, patented the process. It is regrettable that the inventor left this process in the experimental stage. As a matter of fact, his patent lapsed two years later on account of the non-payment of the annual fee. Although it was well known that collodion dissolved in ammoniacal oxide of copper, it was difficult to make a concentrated solution that could be employed on an industrial scale, and which would produce saleable silk having certain invariable physical properties. The " Glanzstoff[1]-Fabriken " of Elberfeld, and later the manufactory of artificial silk at Givet,[2] and others besides, have considered this matter from an industrial point of view.

THE MANUFACTURE OF ARTIFICIAL SILK BY MEANS OF AMMONIACAL COPPER OXIDE.—*Raw Materials.*—Although it

[1] To avoid confusion, we use the name " Despeissis silk " to denote the products obtained by ammoniacal copper oxide, for in a pamphlet of several pages published at Strasbourg in 1900, Director Bronnert of the Glanzstoff-Fabriken of Mulhouse, gives the name " Glanzstoff " also to those threads produced by the zinc-chloride process.

[2] The French patents, held jointly by the Compagnie française de

is true that wood cellulose might be used in the preparation of artificial silk by this method, the most advantageous material to employ on an industrial scale is, as we have already stated, cotton cellulose. The fibrous celluloses of flax, hemp, ramie, and similar fibres have the same chemical constitution, but are mixed or in combination with different proportions of non-cellulose substances. American cotton is chiefly used in the industry that occupies our attention, although some factories buy the waste from carding, combing and other machines used in the cotton industry. This waste is shipped or despatched to the artificial silk centres in bags. It may be mentioned in passing that the long-fibred material, which is the most valuable and important for fine cotton spinning, is not so for the manufacture of artificial silk. Indeed, for this purpose short-stapled cotton would be taken almost as readily as the long-stapled kind. However, experience has shown that the fineness, flexibility and silkiness of the cotton fibres have an influence on the quality of the cellulose. In using, for example, the waste from fine cotton, a better quality of cellulose is obtained than by employing the ordinary short-stapled cotton of Louisiana and Georgia. But the finest, most flexible, and most silky fibres are in general the longest and consequently the most expensive ones.

Soie Parisienne and the Société pour la fabrication de la Soie Artificielle de Givet are—

1. Patent No. 272,718 (1898), for the manufacture of artificial silk.

2. Patent No. 216,625 (1898), for improved apparatus for the spinning and winding of artificial silk.

3. Patent No. 286,692 (1899), for a process of manufacturing cellulose products of great strength and of silky appearance.

4. Patent No. 286,726 (1899), for a process of washing threads, films and other cellulose products in the wound or beamed state.

5. Patent No. 286,925 (1899), for a process of preparatory treatment of cellulose in view of its direct solution.

6. Patent No. 297,278 (1900), for improvements in the preparation of concentrated solutions of copper in ammonia.

7. Patent No. 305,465 (1901), for a process for the manufacture of cellulose having a silky appearance.

8. Patent No. 308,165 (1901), for an arrangement which permits of a simple method of rotating the bobbins on which textile fibres of any kind are to be wound.

9. Patent No. 308,715 (1901), for a process for the manufacture of strong threads of cellulose as a substitute for silk, made from cellulose solution in direct solvents.

These patents correspond closely with those of the " Glanzstoff Fabriken " in Germany.

In order to reduce the net cost, the " Glanzstoff-Fabriken " used the wood of bamboo canes as raw material. The resulting threads were, however, very much inferior to those obtained from cotton cellulose. Bamboo plants, as well as other plants of the same class, contain a large quantity of pecto-celluloses, with a greater or less proportion of ligno-celluloses; the structure of these non-cellulosic bodies is little known. Later, the above firm tried solutions made from paper, but finally returned to cotton cellulose. The grinding of cotton is done by hand, and those who have had considerable experience can judge, by handling the material, of its fineness, length, strength and the degree to which it may be drawn. In the manufacture of artificial silk, however, the difference in the prices of the raw materials is of less importance at the present time than the maintenance and upkeep of the very costly capillary tubes, glass bobbins, etc., and, in general, the mechanism of the works.

Preparation.—Mercerized cotton; cleaning, scouring and bleaching. The cellulose employed for the manufacture of Despeissis silk is cleaned, scoured,

Fig. 6.

and bleached cotton. In the preparation of artificial silk with ammoniacal copper oxide a previous treatment of the cotton with soda and sodium carbonate replaces the usual mercerizing process, and the hydration is effected by boiling the substance under pressure in a kier.

The preparing room has a cemented floor, which is slightly inclined so that the water and other liquids will drain off easily. In Fig. 6, A, A represent two open iron tanks or reservoirs, each of which holds 20 hectolitres (nearly 7 British imperial quarters, nearly 200 lbs.). The outlet pipes of these two tanks join at *a*, and about the middle of the drawing is the plan C of a vertical steamchest or cylinder. Between A, A and C, is a rotary pump D, *see* also Fig. 7, which joins the
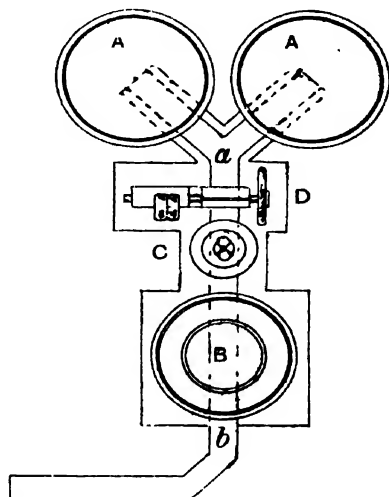
two tanks, A A to the steamchest C by the pipe *a*. This
steamchest is itself joined to a boiling kier B, Fig. 7. The
boiling kier B is approximately the same height as the
steamchest C, but it has a much greater diameter.

A solution of sodium carbonate and caustic soda is placed
in the tanks A, A, Fig. 6 (30 kgs., or 66 lbs., of sodium
carbonate in each tank ; in addition, 50 kgs., or 110 lbs., of
caustic soda for 100 kgs., or 220 lbs., of cotton). The solution
thus prepared is forced into the steamchest C by the rotary
pump D, and is raised to a high temperature by passing steam
through the coil. As the pump D works, the solution fills
the steamchest C, Fig. 7, and then passes through the pipe
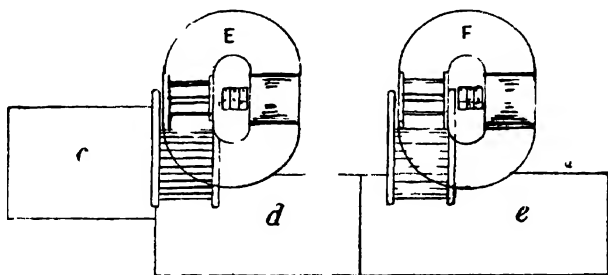
Fig. 8.

X into the boiling kier B, where it mingles with the cotton
in the proportion of 1,000 litres, or 222 gals., of solution to
100 kgs., or 220 lbs., of cotton. When the solution and the
cotton have filled the kier B, the pump D is stopped. A
hinged and flanged cover can be bolted down firmly so that
the whole kier may be made steam-tight. This is done after
the cotton has been placed into the kier ; steam at $2\frac{1}{2}$ atmo-
spheres pressure is then admitted into the kier B. A
thermometer fixed in the cover, and dipping into the liquid,
registers the temperature, which can be regulated at any
moment. A safety valve Y and a steam gauge Z are in
communication with the kier B. ' Attached to the cover is a
pipe that may be opened or closed at will by hand ; this
serves as an overflow pipe for the escape of air and of the solu-
tion which is displaced by the cover when the kier is closed.
A number of perforated iron plates or cages, at equal distances
from each other, support the cotton and hold it in its place

. while the solution is forced through it by the pump D. The
lye circulates continuously during the boiling, which lasts
from 3 to 3½ hours ; the solution passes from the kier B to
the steamchest C through the pipe T T ; returns from C into
B by the pipe X ; passes through the cages of cotton, and
is again drawn into the steamchest C by the pump D. The
cycle of operations is then repeated as often as required.

When the process of boiling in alkaline lyes is completed,
the valve which admits steam into the boiling kier B is closed,
and the solution is withdrawn by opening the valve R. The
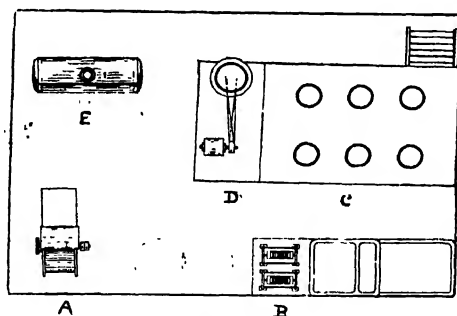
FIG. 9.

hinged cover is then raised, and a quantity of water is poured
on to the cotton, which is firmly pressed against the cages.
This serves as a first washing of the cotton. Then a workman
removes the cotton from the kier B with a hook, and throws
it into wicker baskets placed on wooden shelves which for the
sake of convenience encircle the boiling kier.

Washing.—The cotton is then placed in a wooden tank c, Fig.
8, and from this tank it passes into the washer E, to be washed
with ordinary water. On emerging from the washer the
cotton is deposited into a second wooden tank d. The object
of this washing is to remove the alkaline lye ; the other
impurities are removed only by the subsequent process of
bleaching. After having been washed, the cotton is freed
from water by a hydro-extractor D, Fig. 9, which is fitted
with copper sieves ; the rapid rotation of the cage of the
hydro-extractor removes the water from the cotton in a few
minutes. The cotton is then dried and passed through a
kind of opening machine A, somewhat similar to those used

in cotton-spinning mills, and which has for its object the separation of the fibres. This operation was formerly performed by hand by two workmen, whereas with this opener a single workman can easily open in four hours a quantity of cotton that is sufficient for the production of 350 kgs. (770 lbs.) of silk.

Bleaching.—The cotton that has been subjected to the above-mentioned alkaline treatment must then be bleached, and with this object in view it is placed in six earthenware tanks C, Fig. 9 ; each tank contains a dilute solution of calcium chloride [1] previously prepared in an electrolytic vat B, with a current of 40 amps. 15 kgs., or 33 lbs., of calcium chloride are added to 500 litres, or 110 gals., of water. The cotton remains in this solution in tanks for 5 to 6 hours, and must be stirred from time to time. When this operation is finished, the cotton is passed through the washer F, Fig. 8 ; then it is placed in the wooden tank *e*, and finally freed from water by the hydro-extractor. During this action a stream of water plays into the copper cage for about five minutes in order that the cotton may be further washed during the movements of the hydro-extractor.

Two large store tanks, similar to E, Fig. 9, are provided—one for a concentrated solution of caustic soda, and the other for a solution diluted with water.

When the mercerized cotton is removed from the hydro-extractor it is dried and placed into sheet-iron boxes, each of which has a capacity of about 30 kgs. (66 lbs.). These boxes are then transferred to the mixing tanks, where the cotton is dissolved in ammoniacal copper oxide.

Other methods of bleaching are largely practised, methods which naturally have for their object the purification of the cellulose. These bleaching or oxidizing agents easily attack the impurities which are combined or mixed with the fibrous material, and they do this without affecting the cellulose.

[1] Or calcium hypochloride could be used.

CHAPTER VI

Solutions and Apparatus for Mixing

GENERAL REMARKS ON COTTON TO BE USED IN THE PREPARATION OF THE SOLUTIONS.—Cellulose obtained in this way from raw fibrous materials—*e.g.*, cotton, hemp, flax, ramie—is a white substance distinguished by more or less lustre and translucency, retaining the structural characteristics of the raw materials, of 1·5 sp. gr., and as a chemical individual distinguished amongst CHO compounds by its negative or non-reactive characteristics. The celluloses burn with a quiet luminous flame, leaving inorganic constituents as an ash, retaining more or less the form of the original. In cotton, the average proportion of ash is 0·1 to 0·4 per cent. In the preparation of filter paper for quantitative work it is important to eliminate the ash constituents as far as possible, and this is effected by treatment with hydrofluoric and other acids. "Swedish" filter paper of good quality contains from 0·03 to 0·05 per cent. ash constituents, and constitutes the purest form of cellulose with which we can deal (Cross and Bevan).

In practice it is sufficient to examine the cellulose from the point of view of its percentage composition and its resistance to hydrolysis, its behaviour with solvents and its reactions with sulphuric acid and the nitrating mixture.

The manufacturers of artificial silk buy, in general, cotton ready prepared for solution, and they demand from the bleacher guaranteed limits of moisture, ash and grease. The moisture must not exceed 6 per cent., and the grease and ash combined not more than 0·4 per cent. It is also wise to ascertain the quantity of chloride of lime which has been employed for the bleaching process. This quantity is, in general, 5 kgs. for 100 kgs. of cotton (11·02 lbs. for 220·4 lbs.).

SOLUTIONS

Ammoniacal Copper Oxide

Dissolving of Cotton. Mixing Tanks. Filtration.

Copper Oxide.—Oxide of copper is obtained by the action of oxygen on copper.

Ammonia.—Ammonia is a gas with a characteristic odour. The solution of ammonia in water is termed simply ammonia.

Cuprammonium Solution.—This is a solution of copper oxide in ammonia. It is a blue liquid known to chemists as Schweitzer's reagent, and has the property of dissolving cellulose. It is also called "ammoniacal copper oxide," and "ammoniacal copper." These expressions are synonymous.

Solution of Cellulose in Ammoniacal Copper Oxide.—This solution is obtained by dissolving cellulose in ammoniacal copper oxide. It is a blue viscous liquid that forms the basis of a process of artificial silk manufacture. The cuprammonium solution attacks cellulose rapidly in the cold, and forms a series of gelatinous hydrates which finally dissolve. In order to obtain a good spinning solution, the copper-oxide solution is prepared in the factories under the following special conditions.

The apparatus employed is a vertical cylinder A, Fig. 10. Small pieces of pure copper are introduced through an opening B into the cylinder A. The empty spaces between the heaped-up particles of copper are filled with ammonia, which enters by the pipe C. When the cylinder is full, the opening B is closed, and an air pump working at a pressure of about two atmospheres agitates the solution by internal circulation. In order to have control over the action, it is best to provide each cylinder A with a meter or with a mercurial gauge, so
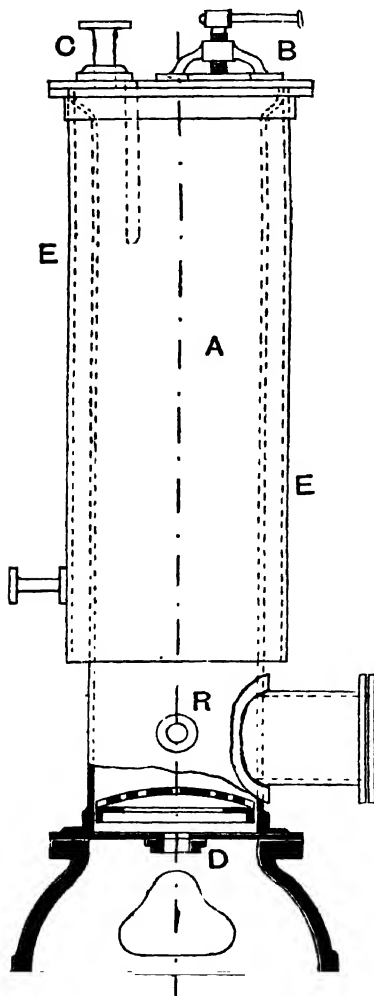
Fig. 10.

that the quantity of air passed through in a given time may be noted.   By C. R. A. Wright's method the speed of the air is regulated in such a manner that in one hour about forty times the liquid volume is allowed to pass through the column.

The solution remains in the cylinder A until it reaches the desired strength, which is measured by a hydrometer.   To this end a gauge is provided through which a few centimetres of copper dissolved in ammonia are allowed to pass.   When the liquid has attained the required degree of concentration, it is allowed to pass through the opening D into a graduated tank, the exact capacity of which is known.   During the time that the copper oxide is dissolving in the ammonia, the temperature in the cylinder A must be between 4° and 6° C. (39·2° and 42·8° F.).   This temperature is regulated by means of a thermometer, which is fixed in the cylinder and dips into the solution.   In order to maintain this approximately constant temperature, the cylinder A is surrounded by a double cover which is protected by insulating materials.

The ammoniacal solution of copper oxide is prepared very gradually, and in order to arrive at the desired density it is necessary that the operation should occupy about 18 hours. Although we say that 18 hours are necessary to prepare properly the solution, it is not an absolutely hard-and-fast rule.   The actual time occupied may be more or less, influenced as it is by the kind of ammonia used, by the combined surface area of the copper presented to attack, etc.   For example, if the copper has not been attacked by a preceding oxidation, and if the apparatus is new and being used for the first time, it is quite possible that the time required may be even 36 hours.   This has been observed several times when using new apparatus.   The time taken, however, has no influence on the quality of the solution, provided the work is carried out under the proper conditions of temperature, pressure and density.

In some works the copper oxide is prepared by intermittent operations—that is to say, after the apparatus has been in operation about three hours, it is allowed to stand for two or three hours, and so on until the required density is obtained. It is understood that the temperature remains approximately at 4° C. (39·2° F.) during the time that the apparatus is standing, as well as when it is in work.   To secure this constant temperature, a current of cooled water, coming from a freezing machine, is made to circulate between the two covers or

jackets of the cylinder A. The cylinder is charged with a fresh supply of dissolved copper every ten days.

The ammoniacal copper oxide prepared in cylinder A, Fig. 11, is run into the graduated reservoir B, so that the quantity may be determined ; then it is transferred from the reservoir B to the mixing tank C—the reservoir for dissolving the cotton. The mixing tank C is a large horizontal iron cylinder in which is an agitator revolving at 55 to 60 revs. per min., thus keeping the ammoniacal copper oxide in motion, and
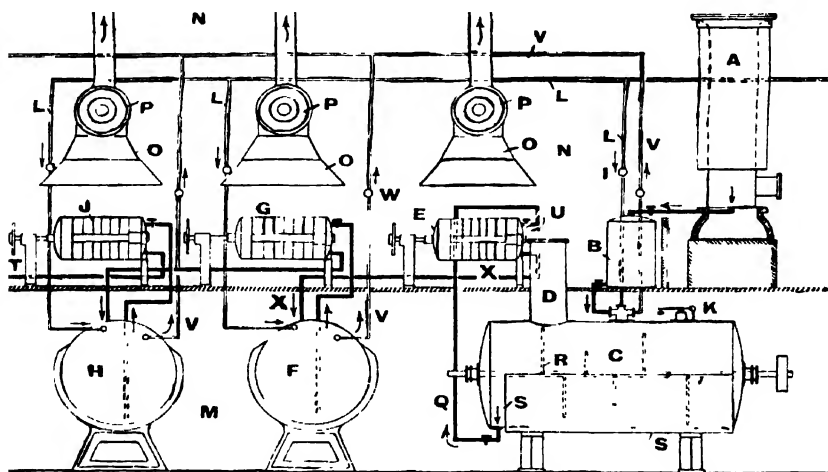
Fig 11.

facilitating the solution of the cotton. Although this mixing tank is situated in the basement to avoid extreme variations of temperature, it is, in addition, provided with a double cover, in order that the solution which is present may, by cooling, be kept constantly at the temperature of 4° C. (39·2° F.). On the mixing tank C is a dome D with a manhole through which the cotton is introduced into the mixing tank. This opening is provided with a lid or cover that may be closed rapidly and fastened down. When the copper oxide dissolved in the ammonia is in the mixing tank, and before introducing the cotton, a very small quantity of a solution of caustic soda is added to the solution ; the whole is stirred for a minute, and then only, while the agitators are in motion,

is the cotton introduced. The usual quantity is from 7 to
8 kgs. (15·4 to 17·6 lbs.) of cotton for 100 litres (22 gals.) of
solution. These quantities, however, may be varied according
to the moisture which the cotton contains, and even according
to the humidity of the surrounding atmosphere.

If the solution is properly prepared, the cotton must be
completely dissolved, and must " draw out " or spin after
having been worked seven hours. It has been shown by
practice that the rapidity with which the cotton dissolves
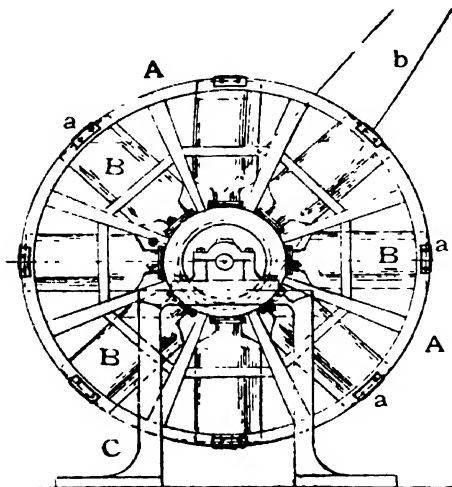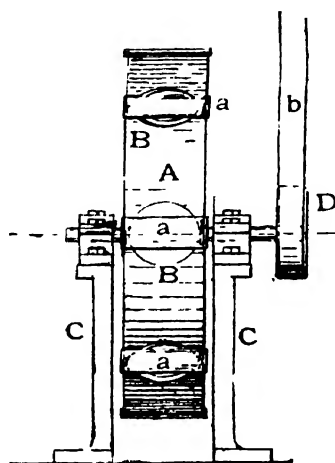
FIG. 12.   FIG. 13.

increases with its degree of whiteness or of bleaching ; the
process of solution might take even 25 hours if the cotton
has not been sufficiently bleached.

Each installation comprises also a mixing tank for exper-
imental purposes ; this is illustrated in Figs. 12 and 13, which
show respectively side and front elevations. The flagons or
vessels B, B are supported by little thongs on a wooden flyer
or cage A. The latter is placed between, and mounted on,
two supports C, and rotated by a belt b which passes around
the pulley D. This flyer turns at the rate of 50 to 60 revs.
per min., and the solution, which fills four-fifths of the vessels
B, B is agitated until the cotton contained therein is dissolved.

We have stated above that the solution " draws " ; this

word indicates a satisfactory degree of fluidity of the solution. The degree of fluidity is of so much importance that the chemist or director of the establishment must test it himself, and not leave this task to the foreman. The correct degree of fluidity may also be determined by pouring 4 or 5 cubic centimetres of the solution into a glass-stoppered bottle ; then by holding the bottle upside down, it can be seen if the solution flows slowly so as to form a continuous thread or thin streak. If, on the contrary, the substance drops or forms an intermittent thread, it has not attained the degree of fluidity that is necessary for spinning.

This degree of fluidity may also be determined in a more accurate manner. For example, a viscometer or graduated glass tube tapering to a point at the bottom, is filled with the solution ; then by noting the time that it takes to run out a given quantity of the different solutions, it is possible to construct a table of reference which would indicate the fluidity of such solutions. It is a good practice to note daily the fluidity of the solution that is being prepared for spinning.

The fluidity must also be ascertained during the mixing. To this end the manager from time to time makes trials to determine, as we have indicated, if the cotton is dissolved or not, and if it is time to stop the agitators in the mixing tank.

When the solution of the cotton is complete, the spinning solution begins to decompose, unless it is kept at a low temperature. It is not easy to determine very exactly the moment when the process of solution stops, and when the decomposition begins ; however, the exact determination of the time of this change is of little practical importance, provided that the solution is kept cool. Whatever may be said to the contrary in certain patent specifications it is not true that a low temperature completely prevents the decomposition of the solution ; no temperature can entirely prevent this action— it can simply delay it for a few days, or rather, perhaps, a few hours. A certain amount of liquefaction attends this decomposition, and this may be found by determining the fluidity as we have stated above. The qualities of a good thread (for example, its strength, elasticity, silkiness and lustre) depend largely upon the condition of the liquid ; indeed, it may truly be said that in proportion as decomposition and lique-, faction advance, the qualities of the thread disappear. It is, therefore, necessary to have a certain degree of uniformity

Fig. 14.
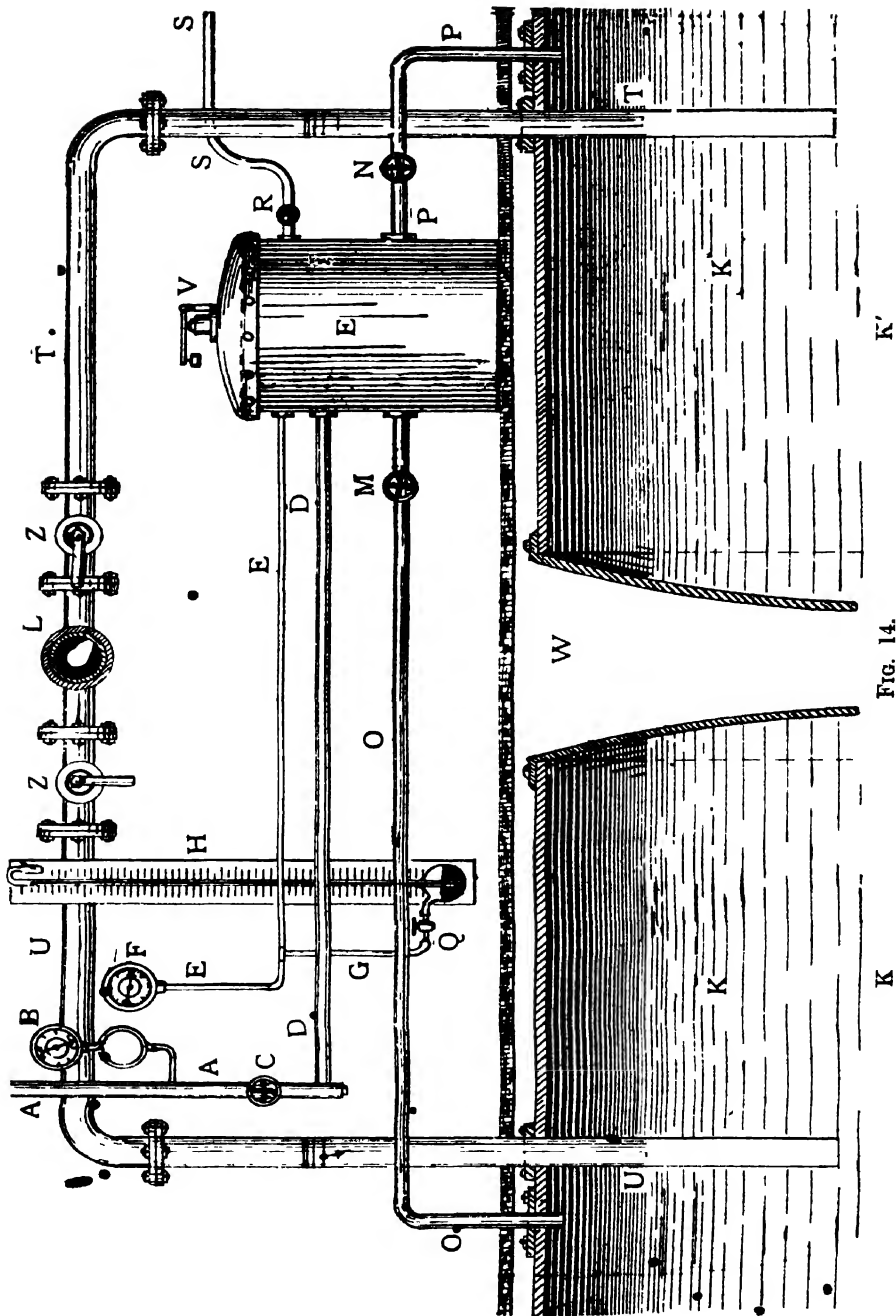
in the silk solution, and to attain this result it is advisable not to allow the solution to get old, but to spin it within three or four days.

Let us return now to the description of the mixing tank, Fig. 11. In addition to the dome D, this apparatus is provided with a safety valve K, and a pipe L for the introduction of compressed air. When the air acts on the surface of the solution, it forces the liquid through the pipe Q into the filter press E. After passing through the filter press E, the solution traverses the pipe X, and is then discharged into the tank F. The filter press E is provided with wire meshes or gauzes, and the solution is thus filtered and freed from most of its impurities. By a similar operation the solution is then forced by air pressure from the tank F, through a second filter press G, into the second tank H. From the tank H it passes through a third filter press J, provided with very fine wire gauzes. This completes the filtering process, and the solution then passes through pipe T, into the large tanks K, K', Fig. 14, of the spinning room.

The tanks F and H, Fig. 11, are used only as intermediate reservoirs for facilitating the process of filtering. It will be understood that to filter this solution, and to make it pass from one tank to another in the manner described, it is necessary to have a complete system of valves, as well as admission and exit pipes for both the solution and the compressed air.

The control of the valves is very important—so much so that it can be entrusted only to a conscientious foreman. In order to facilitate the correct working of the apparatus, the different pipes and their corresponding valves are painted in different and distinct colours ; for example, the exit pipes and valves for the solution are painted in blue, all the pipes and valves for the entrance of compressed air in red, and so on.

The method of operating the valves is somewhat as follows : A quantity of the solution ready to be spun is contained in the mixing tank C, Fig. 11, and must be filtered and conveyed into the tank F. To commence with, we will suppose that all the valves are closed. The valve I is opened first, so that the compressed air may be admitted to force the solution out of the mixing tank C and up the pipe Q. At the same moment, or immediately after, valve L is opened ; this valve is clearly the exit valve from the mixing tank C, and also the admission

valve to the filter press E.   The solution passes through the
filter press E, and then through the pipe X into tank F.   The
valve W for the discharge of the compressed air from the
tank F must, naturally, be open during the time that the
liquid is passing from mixing tank C to tank F, so that no
opposition will be presented to the flow.   Similar operations
are repeated for the transference of the solution from tank F
to tank H through the filter press G, as well as from the tank
H to the large tanks K, K' of the spinning room (see Fig. 14).
   The whole of the manipulation of the valves is performed
from the ground floor N, Fig. 11, it being thus unnecessary
for the operative in charge of this work to descend into the
basement where the apparatus is situated.
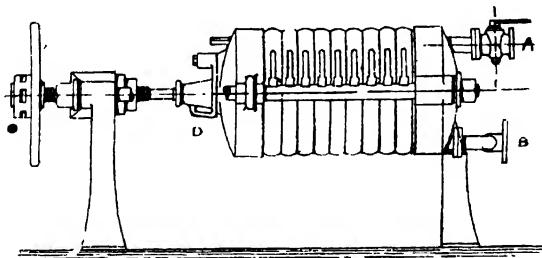
FIG. 15.

Filter Press.—Figs. 15 and 16 show a front elevation and
plan of a filter press, and Fig. 17 is an end view.   The filter
press is composed of a series of metal frames, Fig. 18, over
which are stretched sheets of wire gauze.   These frames, each
one of which is provided with two sheets of gauze, are strongly
bound together so as to form a hermetically sealed box.   The
solution enters the filter press by valve A, Fig. 15, and passes
out by means of outlet pipe B.   The wire gauzes increase in
fineness in the successive presses ;   thus, the first press E,
Fig. 11, contains gauze made from No. 120's wire ;   the second
press G, 140's wire ;   while 150's wire is used in the third
press J.   For the very finest artificial silk it is advisable to
employ a fourth and smaller press, the frames of which are
covered with gauze made from No. 180 to No. 200 wire.
When the solution is good, and the first two filter presses are
in good condition, wire gauzes of the same fineness may be
used for the third and fourth presses.

The first filter press must be opened and examined every two days; the second press every eight days; the third every ten or fifteen days. This operation is performed by rotating the hand-wheel, which withdraws the part D, Figs. 15 and 16, and thus removes the pressure. Each frame can then be cleaned with a very fine brush, and the damaged or loaded gauzes removed and new ones put in their place. In general, however, the wire gauzes get damaged only by inattention on the part of the workman or foreman who has charge of the working of the taps. The damage to the wire gauze usually proceeds from a current of compressed air which, in passing through the network, sets up a vibration in the stretched gauzes, and tears, or rather ruptures, them. To prevent such an occurrence, the workman who is in charge
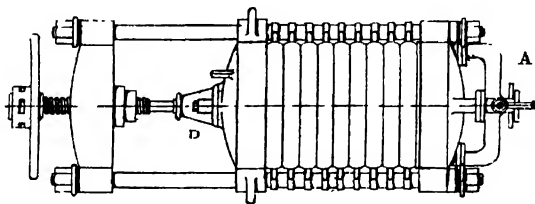
FIG. 16.

of this apparatus must examine the "water levels" of the tank from time to time to see that the solution does not descend to the extremity of the pipes, otherwise the compressed air may have a free passage. However, if it be desired to avoid the trouble of descending too often to the basement to control the levels, a chronometer may be used by means of which, if the quantity of solution which passes through the pipes in a given time be known, almost the same accuracy may be obtained. If only a rupture or break in the wire gauze is caused by the passage of the current of air through the filter press, it may be due to the use of imperfect or inferior quality of gauze. But it is easy to see that when a wire gauze is broken the liquid is imperfectly filtered, and the undissolved particles, which would be held back by gauzes in perfect condition, may reach the capillary tubes in the spinning room. These capillary tubes would then be partially choked, and the result would consequently be the production of a thread of irregular count, and of bad quality.

In later years, in the manufacture of artificial silk by the cuprammonium process, there has been a tendency to employ only cotton, cleaned and carefully prepared under special conditions.   By this means it is unnecessary to adopt an extended system of filtration, for when the material is pure, well cleaned and prepared, a single filter press, with gauze made from Nos. 150 to 200 wire, will suffice.   Moreover, the ruptures in the filter press, and the resulting obstructions in the capillary tubes, are prevented.

The Viscose factory, on the other hand, try more and more to use wood cellulose.   Satisfactory results have been obtained from pulp made from Norwegian wood, and also from American
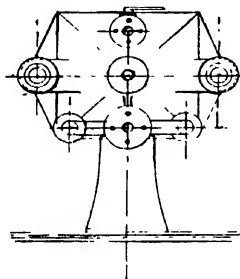
Fig. 17.
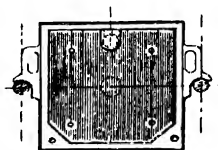
Fig. 18.

ligneous materials which have been prepared specially for this purpose.   The substitution of wood cellulose for cotton is resorted to only to effect a reduction in the price of the finished article.   However, the cultivation of cotton increases every year in order to meet the increased demands for the production of the ordinary fabrics, and for new developments which require cotton cellulose.

With further reference to Fig. 11, the heavy fumes of ammonia, which are evolved during the cleaning of the filter presses, escape through the wooden chimneys O, and these are provided with ventilators P.   The wire gauzes must be fired or burnt before they are used, in order to remove all impurities, grease, etc., which may be adhering to them. The charged wire gauzes from the frames of the filter presses are washed in ammonia, and may be used a second time after having been dried and fired.

It may be said in passing that each establishment should be provided with one or two respirators or diving apparatus

in order that the workman may descend into the basement, in the case of an accident, without danger of being asphyxiated. For example, a pipe might burst, or a joint or valve might leak, and then it would be impossible to approach the leakage without a respirator, so that in the absence of such an apparatus at a critical time the whole of the liquid might run to waste.

Within recent years the foregoing type of filter presses with wire gauges has been supplanted by filters such as that illustrated in Fig. 18a. This is Buhring's patent and made by La Compagnie Générale de Filtrage of Paris. The apparatus embodies *inter alia* a closed cylinder which contains a special filtering medium. Three valves are provided at the top of the cylinder, and three other valves near the base. The solution to be filtered enters by one of the upper valves, passes through the filtering medium, and leaves the cylinder by one of the lower valves.

The cleaning of the filter or of the filtering medium is accomplished by a stream of water which enters one of the lower valves, flows upwards or in the reverse direction to that followed by the solution, and escapes out of one of the upper valves. A simple alteration of the valves enables this cleansing operation to be conducted without any displacement of parts, thus effecting a great economy in labour. An air valve is also provided at the top of the cylinder.

The filtering medium is little affected by the operation, hence its use is more economical than that of wire gauzes ; the latter have to be replaced pretty often. Such filters as that illustrated in Fig. 18a are usually arranged in series, so that while one is being cleaned the others can be in work.

Other machine makers have introduced apparatus designed to meet the difficulties encountered by the use of the older types of filter presses ; for example, attempts have been made to filter solutions of cellulose by centrifugal action in some form of hydro-extractor, but so far as we know, this method has found no practicable outlet.

We now come to the tanks K, K′, Fig. 14, from which the solution is conveyed to the main pipes L of the spinning room. Suppose that the tanks K, K′ are full of solution which is ready to be transformed into artificial silk threads. Compressed air at about four atmospheres is introduced through the pipe A, the actual pressure being indicated by the

Fig. 18a.

pressure gauge B. When the valve C is open, this compressed air passes through the pipe D into the air tank E, which is provided with a safety valve V. From tank E two pipes O and P lead to the tanks K, K'. It is therefore only necessary to open the valves M or N in order that the pressure in E may be communicated to the surface of the liquid in K or K'. This pressure on the face of the liquid in K or in K' forces the solution up the pipes U or T, both of which are connected to the pipe L. This pipe forms part of the main pipe of the spinning frame. It need hardly be said that the pressure on the liquid on these tanks K, K' diminishes as the solution is forced into the main pipe L, unless provision is made for keeping it constant. The pressure should be constant in order that a regular thread may be produced. A pressure of four atmospheres is quite unnecessary for spinning the solution ; a constant pressure of 1700 mm., which is indicated on the open pressure gauge H, is sufficient for the spinning of a fine regular thread.

This almost constant pressure is obtained in the following manner : As far as the valve C, which is closed, there is, as we have already stated, a pressure of four atmospheres, whereas in the tanks K, K' there is a pressure of only 1700 mm., indicated by the open pressure gauge H. If now this pressure on the surface of the solution in K, K' falls, for example, 5 mm., the open pressure gauge H will indicate 1695 mm. ; the required increase of pressure (i.e., 5 mm.) can be obtained by opening slightly the valve C until the open pressure gauge again registers 1700 mm. The same operation must be performed for each diminution of pressure, and the interval between the operations depends upon the rate of flow of the solution—this interval is, in general, from two to three minutes. By the above means an approximately constant pressure is exerted on the solution.

A conscientious workman has charge of this duty, and he should never leave the post without being relieved by another equally careful attendant. The quality of the artificial silk depends to a great extent upon the careful attention of the man to whom this work is entrusted. We may add that the valve C (Fig. 14, p. 43) must be opened gently and carefully, for a sudden movement is apt to open the valve too much, in which case the consequent variations in pressure would result in thick places in the thread. The workman should

keep his hand on or near the valve wheel C ready to check any change of pressure which might result from the breaking or tearing of an indiarubber tube. It is possible to employ automatic regulators of pressure.

The pressure of 1700 mm. is not an absolutely fixed pressure for all solutions ; the pressure is dependent somewhat upon the constitution of the cellulose, the count of the yarn which it is desired to spin, the size of the opening of the capillary tube, and the surface speed of the winding bobbins.

The two tanks K, K', Fig. 14, are provided with gauges or levels which indicate the height of the solution, and it is a wise plan to keep the tanks about half-full, for when they are nearly empty, the compressed air enters the pipes U and T, and then reaches the main pipe L of the spinning room. It is then impossible to produce satisfactory artificial silk, for the thread, on emerging from the capillary tube, is subject to numerous interruptions caused by air bubbles that are ejected at the same time. In order that the tanks K, K' may, during work, be about half-full of solution, it is necessary to withdraw the solution from them alternately. Suppose the tank K' is in operation, valve N is open, and allows a free passage for the compressed air which forces the solution up the pipe T and into the main pipe L, provided, of course, that the valve Z is open.

Let us assume that the level of the solution has fallen a little below the half-way line in the tank K' ; it is then necessary to allow this tank to remain inoperative, and to commence using the solution in tank K without interrupting the spinning process. The change is performed by opening the valve M, which offers a clear course for the compressed air, and the solution immediately ascends the pipe U as far as valve Z, which is closed. During this time it is naturally essential to watch that the pressure does not fall, because a much greater amount of compressed air is necessary. When the valve Z is opened, the solution reaches the main pipe L by both pipes T and U at the same time, and the work is therefore being carried on for an instant by the joint action of tanks K and K'. If now valves N and Z be closed, the tank K' is shut off from communication with the main pipe L, and the liquid is delivered only through pipe U. As the rate of flow is known, it is now possible to refill the tank K' with solution.

However, if it so happens that for the sake of repairs, or for any other cause, one of the tanks K, K′ is for some days unfit for service, it will be necessary to work with a single tank. This is done in the following simple manner : All the operations are the same as before up to the filling of the tank (K′, for example) when the latter is not quite half-full. In order to refill it while it is still working, the valve C is shut throughout the operation, so that the compressed air from the pipe A cannot enter the tank E. At the same time the operation of filling the tank K , which is supplying the liquid to the main pipe L, is commenced by conveying to the tank fresh solution under a pressure of four atmospheres. The level of the liquid rises, and the compressed air between this level and the walls of the tank occupies a gradually decreasing volume, while the pressure on the surface of the solution rises proportionately unless means are taken to avoid this increase in pressure. This is done by opening the release valve R, which allows the excess of compressed air to escape through the pipe S into the open air, and thus keeps the pressure at its constant value. Thus the reading of the open pressure gauge H will be approximately 1700 mm. From observations it is found that 1800 litres (396 gals.) of solution produce at least 100 kgs. (220 lbs.) of artificial silk. This amount is, however, only a mean value—the actual value will vary according to the nature and density of the cuprammonium solution employed, and above all to the percentage of cellulose in solution, and also the hygroscopic state of the cellulose at the time of solution.

CHAPTER VII

The Spinning Mill

THE thread, in the form of yarn, is the result of the coagulation or solidification of viscous jets of cellulose solution squeezed or forced out of the narrow openings of specially constructed tubes called spinnerets or capillary tubes. The tubes are partially immersed in a liquid capable of facilitating the coagulation or precipitation of the substance. This coagulation is accompanied or followed by the elimination of the reagents which have been used by washing in baths containing suitable solvents.

The manufacture of artificial silk is an ingenious imitation of a natural process, for the thread of the silkworm passes through the following three phases, which also characterize the operations of the artificial silk spinning machine—

(1) Passage of the viscous liquid through the spinnerets or organs situated at the mouth of the animal.

(2) Coagulation or solidification of these jets in the form of threads on exposure to the air.

(3) The rolling or winding of the threads into a cocoon.

The term " spinning," although in general use, is not really the designation which should be applied to the manufacture of artificial silk ; the Germans employ the term " Fadenzie-herie " (wire-drawing), which appears to be more appropriate.

In the process that we are going to describe, the coagulation of the material is effected by contact with acids or alkalies.

Acids.—The acids in question are the corrosive liquids of which the prototype is sulphuric acid or vitriol.

Alkalies.—The alkalies or alkaline bases, also termed alkaline lyes, are the very caustic and colourless liquids of which the prototype is sodium hydroxide, also called caustic soda, caustic-soda lye, soda lye, caustic lye, or, for short, simply soda.

Résumé of the manufacture of artificial silk by the Despeissis or cuprammonium process : The original material is cotton cellulose which is dissolved in ammoniacal copper-oxide solution. The solution thus obtained is stored in a tank from which it is expelled by air pressure through capillary tubes or spinnerets, the opening of which is determined by the size of the

desired jet of liquid, and by the degree of tenuity which it is desired to communicate to the thread which is formed by coagulation.

On leaving the spinnerets the jets of viscous cellulose dissolved in Schweitzer's reagent (ammoniacal copper oxide) pass through a special chemical bath, the action of which is to solidify instantaneously the cellulose in solution, and so produce a substance circular in section, and similar in appearance to yarn, and at the same time to remove part of the copper and the ammonia which are carried forward by the substance. From this point a suitable mechanical arrangement of pulleys, drums and bobbins, or some similar parts, draws the threads through a dilute acid bath. The time taken to pass through
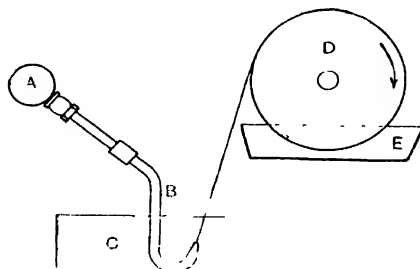
Fig. 19.

this bath is sufficiently long to ensure the removal by chemical action and osmosis of practically all the copper and ammonia.

The threads emerging from the capillary tubes unite again by simple adhesion, but not as a single solid substance. When the filaments of artificial silk thus obtained are well purified by methodical washings, they are dried on bobbins by means of a current of warm air.

Fig. 19 is an enlarged view of the parts that operate immediately before and after the thread is formed, and in which A indicates the distribution pipe through which the cuprammonium solution of cellulose under pressure passes to the capillary tubes ; B, the capillary tube or spinneret, from the small opening of which the viscous liquid emerges in the form of a thread ; C, the shallow bath that contains the acid or alkaline solution for instantaneously coagulating the substance ; D, the bobbin upon which the thread is wound ; and E, the bath containing a weak acid.
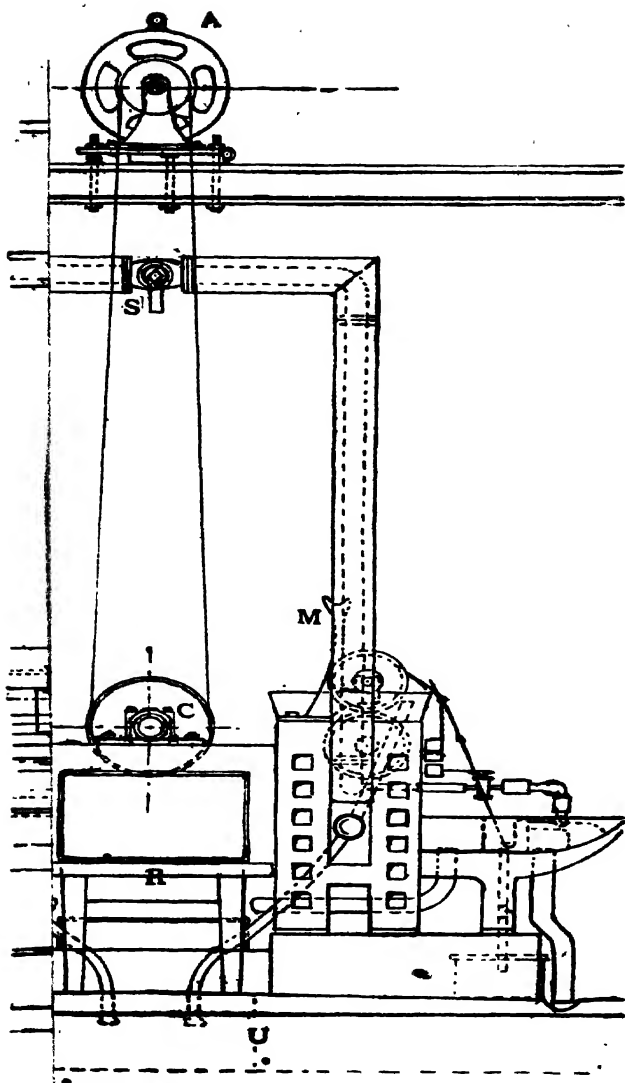
Fig. 21.

Removal of the Copper.—The object of this operation is that of eliminating the copper from the thread. When acids are used as agents for coagulation, the copper is removed in the first bath C, Fig. 19, and at practically the same moment as solidification takes place. The thread as it issues from the spinneret is blue, but is colourless when it leaves the coagulation bath C. In every case the thread still contains copper when it leaves bath C ; it is therefore made to pass through a second bath which contains water slightly acidified. Thus, the thread on bobbin D is immersed for some time during its rotation in the bath E.

In the case of coagulation by alkalies there is no removal of copper, properly speaking, in the coagulation bath. When the thread leaves the bath it is blue in colour, due to the precipitation of cupric cellulose. Therefore, after being washed with water it must pass through an acid which removes the copper and leaves the thread colourless.

Washing.—It is sufficient to wash the bobbin (formed as in Fig. 19) in water to remove the acid left in the threads after emerging from bath E ; this done, the artificial silk thread is complete, and needs only to be dried and wound into hanks or other suitable form. The Despeissis method of preparing artificial silk is as simple as it is complete, and by following this process anyone can produce threads of artificial silk without having very complicated apparatus at his command. The manufacturing process is complicated a little, however, by the mechanism which is essential in large industrial establishments.

Description of a Spinning Room—Figs. 20 and 21 show respectively front and side elevations of an artificial silk spinning machine, while Fig. 22 is an enlarged view of a small part of Fig. 20, and Fig. 23 is a section of the latter taken through the line A·B. The solution from the tanks K, K', Fig. 14, reaches the main pipe L, Figs. 20 and 21, from which branches pass to the end of each spinning machine. These pipes L, which conduct the solution, and which are represented by dotted lines in Figs. 20 and 21, are made of iron ; in some works they are made of glass or of porcelain. In all cases they are covered with insulating material in order that the solution which is passing through them may be kept at a constant temperature of 4° to 5° C. (39·2° to 41° F.), whereas the temperature of the room may vary from 17° to 23° C.
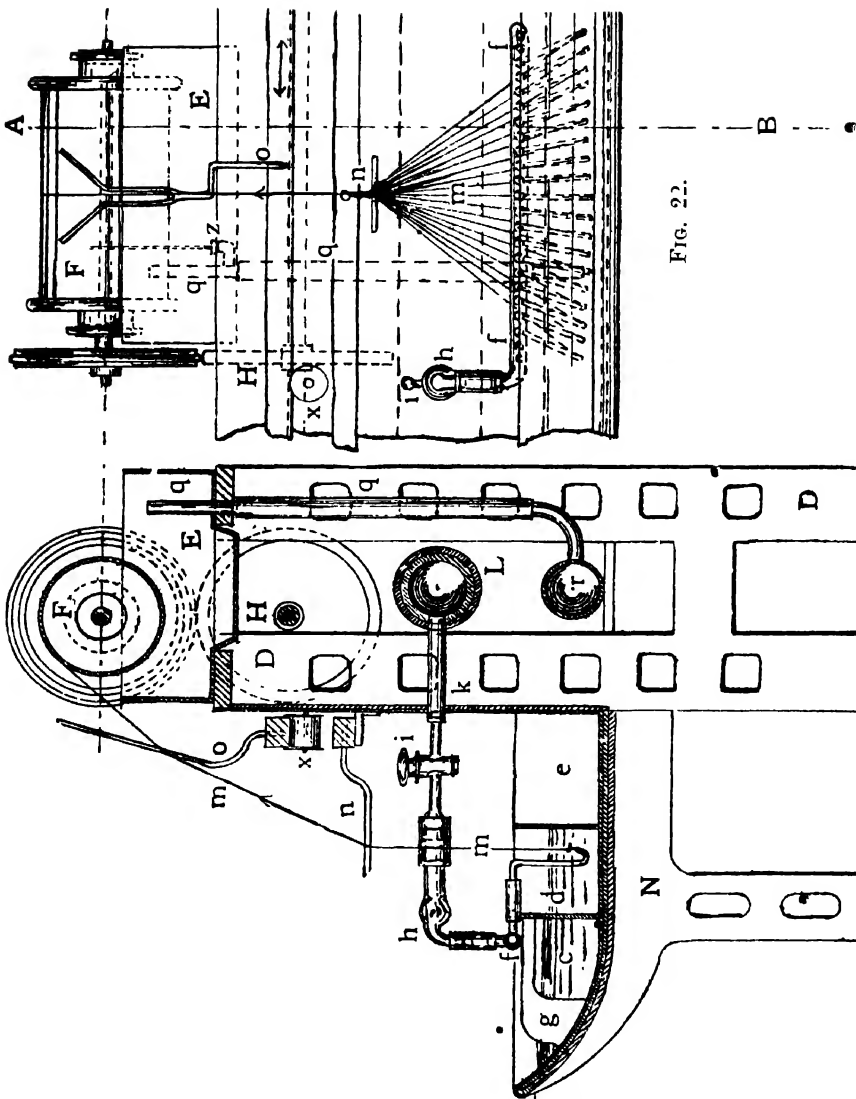
Fig. 22.

Fig 23

(62·6° to 73·4° F.). It is better, however, to maintain a constant temperature of, say, 63° F. Projecting from the pipe L, Fig. 23, which extends the whole length of the machine, and at equal distances along it, are several short pipes, which are connected by rubber sleeves or tubing to glass taps i. Each tap when open allows the solution to pass through a second rubber sleeve, then through the bent tube h, and the
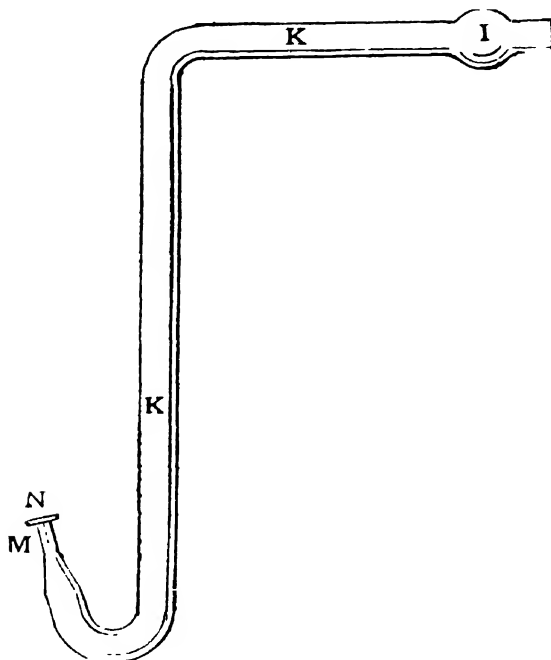
Fig. 24.

glass or lead distributor f, and finally through a number of glass capillary tubes which are supported by the distributor f.

Fig. 24 is an enlarged view of one of these capillary tubes, and the end of each one is immersed in sulphuric acid, which is contained in a leaden trough d, Fig. 23, extending from one end of the machine to the other. The trough is kept about three-quarters full of the acid. The threads m from each distributor f are collected together by the glass guide n, Figs. 22 and 23, and then pass through a second thread guide o before being wound on the hollow glass cylinder F. The

upper thread guides *o* are fixed to a long rod which is supported by, and free to move laterally on, the anti-friction rollers *x*. The horizontal to-and-fro movements of this bar carry the thread guides *o* from side to side of the glass cylinder F as in ordinary warp-winding machines. The bar, and consequently the thread guides, as well as the glass cylinders F, receive their motion from a motor *A*, Figs. 20 and 21, suspended on the rails B´; the rails are fixed to the feet or frame of the motor as shown, and thus provision is made for keeping the belt tight. The motor A communicates its motion to pulley C by means of a belt. This pulley makes 125 revs. per min., and by one of the well-known systems employed for winding,
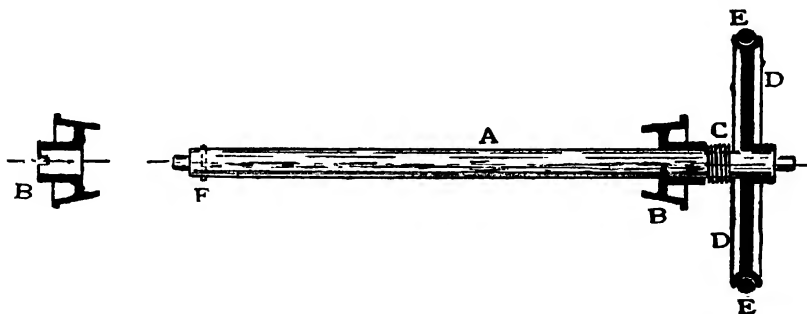
FIG. 25.

imparts a circular motion to the cylinders F, and a to-and-fro movement to the thread guides.

Each bobbin or cylinder F rotates partially immersed in dilute sulphuric acid, which fills the leaden trough E three-quarters of its height. In order to support the glass cylinders F, Figs. 20 and 21, to the limit of their movement, they are mounted on shaft A, Fig. 25, which carries at one end a grooved wheel D around which is a rubber band E. Two bronze cones B, B support the glass cylinders between the pin F and the spring C, and provide means for the lowering of the cylinders at the end of each operation by a turn of the hand. The cylinders thus mounted are placed in the supports M, M, Figs. 20 and 21, and they commence to rotate immediately on coming in contact with the frictional driving drums H, which are fixed on a shaft extending the full length of the machine. The pipes *q*, Fig. 23, which join troughs E and pipe *r*, drain the sulphuric acid through the large pipe U, Fig. 21, into a

pit situated outside the building. But the top part of pipe q, Fig. 22, serves only as a waste-pipe or overflow, because the threads m, while being wound on the cylinders, are continually drawing up the sulphuric acid, and the troughs E would be filled in a few hours if the waste pipe were not there to carry away the surplus. If it is desired to empty the trough E completely, it is necessary to take out the cork or plug Z fixed to a rod.

In Fig. 23 it will be seen that there are three different troughs, c, d and e, mounted in the framework N, and each is lined with lead. In the first trough, c, cold water is circulated, and this must cool the sulphuric acid in the trough d to 17° C. (62·6° F.) and keep it at that temperature ; the third trough, e, is provided to receive the broken threads which the workmen throw in after having pieced or joined up a thread. Leaden projecting pieces g are placed at suitable distances apart in the first trough c for the purpose of supporting the distributors f. The threads that emerge from the capillary tubes float in the sulphuric acid d, and are picked up with a copper hook, which the workmen hold in the left hand (seen in Fig. 26) ; these threads are passed through the thread guides n and o and over cylinders F. Figs. 22 and 23 ; then with nickel scissors, which are held in the right hand, the workman cuts off the thick part held on the hook, and the single thread, drawn on by friction, is wound on to the bobbin. However, it very seldom happens that all the 18 threads m, Fig. 22, break at the same time—the breakage is usually restricted to only one or two threads ; in this case the workman lifts with his hook the broken thread which is floating on the sulphuric acid, places it across the other 17 threads, and the latter draw it forward as they are wound collectively on the cylinder. This constitutes the sole work of the piecers. There are, in addition, several young workpeople (doffers) whose duty it is to mount the glass cylinders on the shafts, to bring them to the frame, and to remove them when they are full of artificial silk. It should be stated that the doffing operation takes place while the frame is running ; 'thus, one of the operatives standing on the stool R, Fig. 21, removes the full bobbins G from their supports M, while another one standing immediately in front. of the frame, near the trough c, Figs. 21 and 23, puts an empty cylinder in its place. A workman (piecer) is able to attend from 10 to 15 distributors.
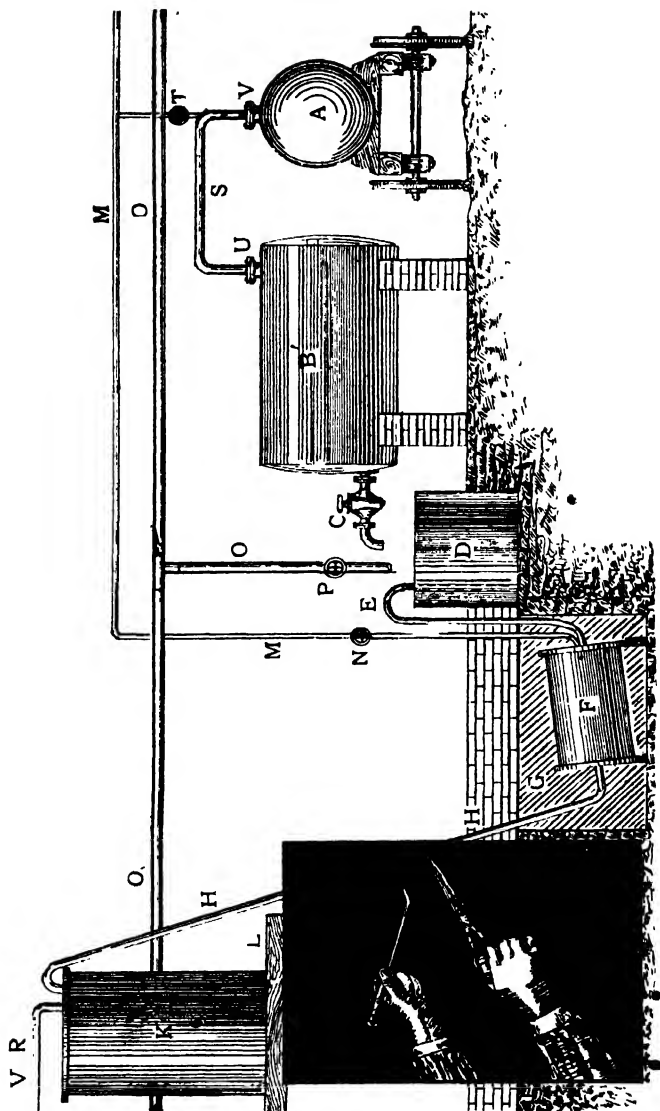
FIG. 28.

FIG. 26.

or even more if the solution is good and the filtration perfect. A double-sided spinning frame, as illustrated in Fig. 21, contains from 60 to 80 distributors. With the object of preventing the threads from intermingling when two or more neighbouring threads break, the capillary tubes are sometimes arranged in a little framework provided with glass partitions, so that each one is in a separate compartment. However, seeing that the breaking of threads is now a rare occurrence, these means of precaution have become practically useless.

Each establishment requires a chief overseer or overlooker, and for each machine a foreman in charge of the cleaning, of the circulation of the cooling water, of the flow of the sulphuric acid, and of the changing of the choked capillary tubes.

The chief overseer is responsible for the speed of the winding, which must be kept at a constant speed of 60 revs. per min.; of the satisfactory winding of the thread; of the piecers' work; and of the upkeep of the machines, the framework of which must be whitewashed with lime twice a week to prevent corrosion by the sulphuric acid. He is, besides, responsible for the proper ventilation, and for the temperature 17° C. (62·6° F.) of the workshop; he superintends the workman whose duty it is to keep the solution at a constant pressure, and exercises a general control over all the workpeople; it is his duty to examine the levels of the tanks, to see that the acid and the solution are kept at the proper temperatures, and to prevent any waste of the sulphuric acid.

In regard to the flow of the acid, it may be said that in a general way this takes place twice a day after an analysis has been made. A boy, under orders from a chemist, brings samples of the sulphuric acid twice a day from the trough *d*, Fig. 23.

With respect to the temperature of the liquid used for the precipitation of the cellulose, it is known that acids of mean concentration when warm rapidly destroy cellulose, and cause an important molecular change which renders the product brittle and pulverulent. The acid must, therefore, be used at a low temperature—at least below 20° C. (68° F.).

Analysis of the Sulphuric Acid.—For the benefit of those who are unacquainted with the process, we describe here in detail the analysis of sulphuric acid. Five cubic centimetres from a sample of sulphuric acid, which the boy brings from
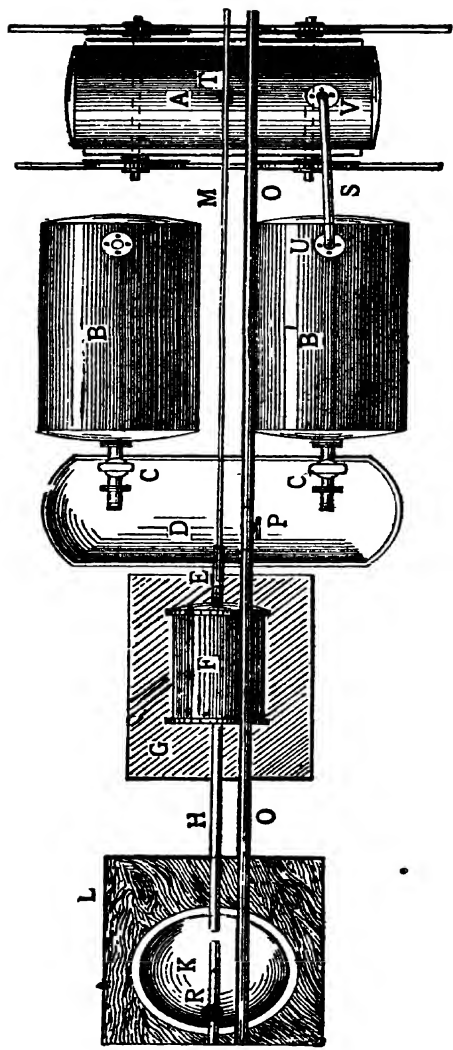
Fig. 27.

the spinning room, are introduced into a flask or beaker. To the 5 c.cms. of acid are added three drops of methyl-orange, which impart a faint red colour. This glass is then placed under a graduated tube which tapers to a point at the bottom (burette), and which contains a solution of sodium carbonate previously titrated (0·0935, for example). The acid and methyl-orange in the flask are kept in motion while the sodium carbonate is added drop by drop. The red or rose-coloured liquid in the flask gradually gets paler as the sodium carbonate is added. At a certain moment the rose-coloured solution turns yellow, and the number of cubic centimetres of sodium carbonate which has been required to effect this change of colour enables one to calculate the percentage of pure acid.

Example : 5 c.cms. of sulphuric acid mixed with three drops of methyl-orange require 31 c.cms. of sodium carbonate before the yellow colour is obtained ; 1 c.cm. of sodium carbonate corresponds to 0·0935 of sulphuric acid (titrated previously) in our particular case.

$$\therefore 0{\cdot}0935 \times 31 \text{ c.cms.} \times \frac{100}{5} = 57{\cdot}970 \text{ per cent. of}$$

sulphuric acid.

By this analysis the spinning overseer can judge whether more acid or more water should be added to the acid solution in the trough d, Fig. 23. An acid diluted to 20 per cent., for example, would not attack the solution sufficiently, and would not produce a thread of the required strength. A thread formed in such a solution would break even before it reached the first thread guide, whereas a thread which had passed through a 90 per cent. solution of sulphuric acid would be burnt completely. It is true that the percentage of the sulphuric acid could also be determined by means of a hydrometer if the trough d did not contain copper hydroxide and ammonia in addition to sulphuric acid and water. However, an able overseer can determine approximately the strength of the acid by observing whether the broken threads float on, or are partially immersed in, the sulphuric acid in the trough d.

When the acid becomes too dilute it is drained through the pipe p, Figs. 20 and 21, into the earthenware vessels P, which are placed under the machine at regular distances apart. With a little earthenware pitcher, of a capacity of ½-litre (⅒ gal.), a workman takes from the vessel P the acid which

has been already used, and pours it into the troughs E, so that the threads which are wound on the bobbins F dip into this diluted acid. The water enters through long indiarubber tubes J, set at convenient distances apart, and joined to the main pipe as shown in Fig. 20 ; at the lower end of each indiarubber tube J is a tap which is brought successively before each trough E within its range in order to supply the necessary quantity of water to the sulphuric acid. About 2400 litres (528 gals.) of acid—per day of 24 hours—are required to produce 350 kgs. (771·4 lbs.) of artificial silk. This consumption of acid is evidently proportional to the quantity of copper and of ammonia to be eliminated from the thread.

The sulphuric acid is obtained from a manufacturing chemist, and is conveyed by train to the works in a large cylindrical tank A, Figs. 27 and 28. With compressed air coming through the pipe M and the valve T, the sulphuric acid is forced from the tank A, through the pipe S and orifice U, into one or other of the two cylindrical tanks B, B[1] situated outside the works. The acid is allowed to run out of these tanks, when required, through large earthenware taps C, C[1] into a long tank D ; here it is diluted with water until the mixture reaches a certain strength, which is determined by analysis or by means of a hydrometer. The water for this purpose is conveyed by the pipe O and valve P. The mixture, thus prepared, is ready for use, and passes as required through the syphon E into a pulsometer F, and from the latter into a tank K placed on a raised platform L. A leaden syphon R in the tank K directs the acid into the trough d, Fig. 21, of the spinning frame. The pulsometer F, Fig. 28, made of ebonite, receives the compressed air through the pipe M and the valve N. A little funnel-shaped orifice, closed by a cork and fixed in the pipe R, serves to start the syphon in the well-known manner.

CHAPTER VIII

The Cleaning of Spinnerets or Capillary Tubes

CAPILLARY TUBES OR SPINNERETS.—The capillary tubes come from glass works in the form represented in Fig. 29 ; they have been drawn out by skilful workmen, and have an opening or bore of from 0·10 to 0·20 mm. diameter. Each capillary tube is examined very carefully with a microscope to make sure that the bore is the exact size required. The glass-blower in the works receives these capillary tubes and cuts them in two at the dotted line M, Fig. 29 ; he then joins each
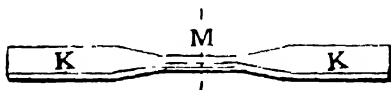
FIG. 29.

extremity K to a longer tube, which is bent as shown at K, K, Fig. 24. After he has blown a small bulb at I, to secure the indiarubber tube which unites the capillary tube firmly with the distributor, he fixes at the other extremity M of the capillary tube a small round disc or plate, N, which is used for the purpose of facilitating the egress of the thread. This dish or plate must be flat and not funnel-shaped, otherwise the flow of the solution would be irregular and more threads would be broken than if the small plate were dispensed with.

When the capillary tubes are choked, say, by imperfect filtration or by badly prepared solution, they must be removed and cleaned. The small invisible speck of powder or foreign matter, which is, however, large enough to close up the opening of the capillary tube of 0·20 mm. diameter, passes through the comparatively wide parts K, K, Fig. 24, and reaches the part M of the capillary tube, which is thus obstructed ; it is then necessary to force the particle back through the end I. To do this the choked capillary tube must be lifted from the distributor and replaced for the time being by one with a free passage ; the glass tap i, Fig. 23, is closed while this change is being effected, unless when the work is performed by a quick

and skilful workman. The choked capillary tube is then sent to the cleaning department ; part of the apparatus used in this department consists of a vessel B, Fig. 30, placed inside a metal pot A which is hermetically sealed. The vessel B is filled with a mixture of one-third sulphuric acid taken from the vessel P, Fig. 20, and two-thirds water ; this mixture is entered into B through the funnel F. Compressed air at about $1\frac{1}{2}$ atmospheres, indicated by the pressure gauge C, is then allowed to act on the surface of the liquid in B, with the
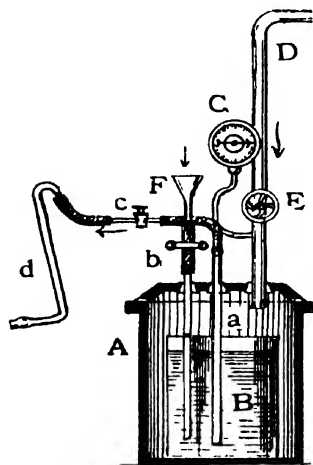
FIG. 30.
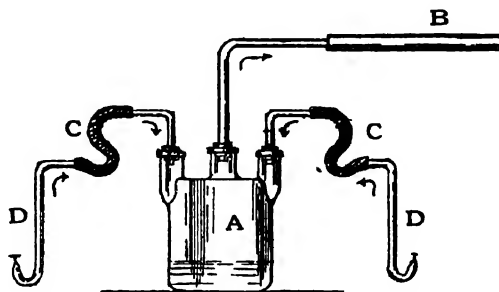
FIG. 31.

result that the liquid rises immediately by the pipe a, as far as the glass tap c. Attached to the end of the tap c is an indiarubber tube, and the small end of the choked capillary tube is entered into this tube as shown in the figure, where all the parts are shown in position for cleaning the tube. It is easy to see that when the tap c is opened the compressed air will act on the surface of the liquid, and will probably force the particle out of the wider end of the capillary tube. If this operation, however, does not dislodge the matter, the other end of the capillary tube D, Fig. 31, is fixed to a bottle A by the indiarubber tube c as shown. By creating a vacuum in this bottle by means of a pump attached to the pipe B, the solution is withdrawn from the capillary tube and falls into the bottle A. One or two workmen then finish this

cleaning process by agitating the capillary tubes in warm water ; the capillary tubes are then dried and returned to the spinning frame ready to be used again. In ten hours two or three workmen should be able to clean in this manner 200 to 300 choked capillary tubes, and to return them to the spinning department. The spinning frame attendants who change the choked capillary tubes are provided with indiarubber finger-stalls, which are furnished by the manufactory at a low price.

CHAPTER IX

Washing, Filtration of Water, and Soap Washing

WASHING.—A series of washings, for the most part with water, is necessary to free the thread from the acid used for the removal of the copper. At the end of each doffing, the winders take the full glass bobbins, the threads of which are impregnated with sulphuric acid, and place them on the bobbin carts, Fig. 32, in an adjoining building—the washhouse. Here the bobbins are placed in wooden banks or creels, and the silk is washed for six hours in acetic acid or formic acid mixed with ammonia, the whole greatly diluted with water. The following is a detailed description of the various
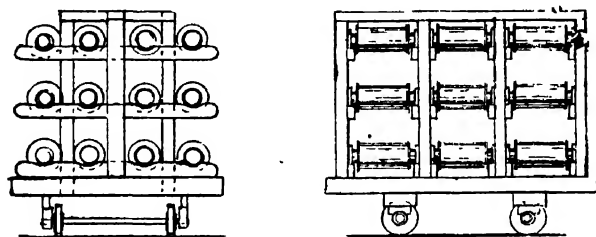
FIG. 32.

stages in the operation of washing, and the solutions used in the process: When the carts, Fig. 32, are filled with the glass bobbins, they are brought on to the rails M, Fig. 33; the bobbins are then placed on the double-staged racks or tables H, so arranged to occupy a minimum amount of space. The workmen in this department bring the bobbins from these tables and put them into a kind of wooden creel or bank, illustrations of which appear in Figs. 34, 35 and 36, showing respectively elevation, an enlarged plan of part of one row, and an enlarged end view; while Fig. 33 is a plan of the apparatus in the washhouse. In each vertical row of the bank there are six bobbins, say, I, II, . . . VI., four of which only are shown in Fig. 36, but all six appear in each row in Fig. 34. To the right of the apparatus in Fig. 33 are five stoneware tanks, A, containing the liquid for washing the

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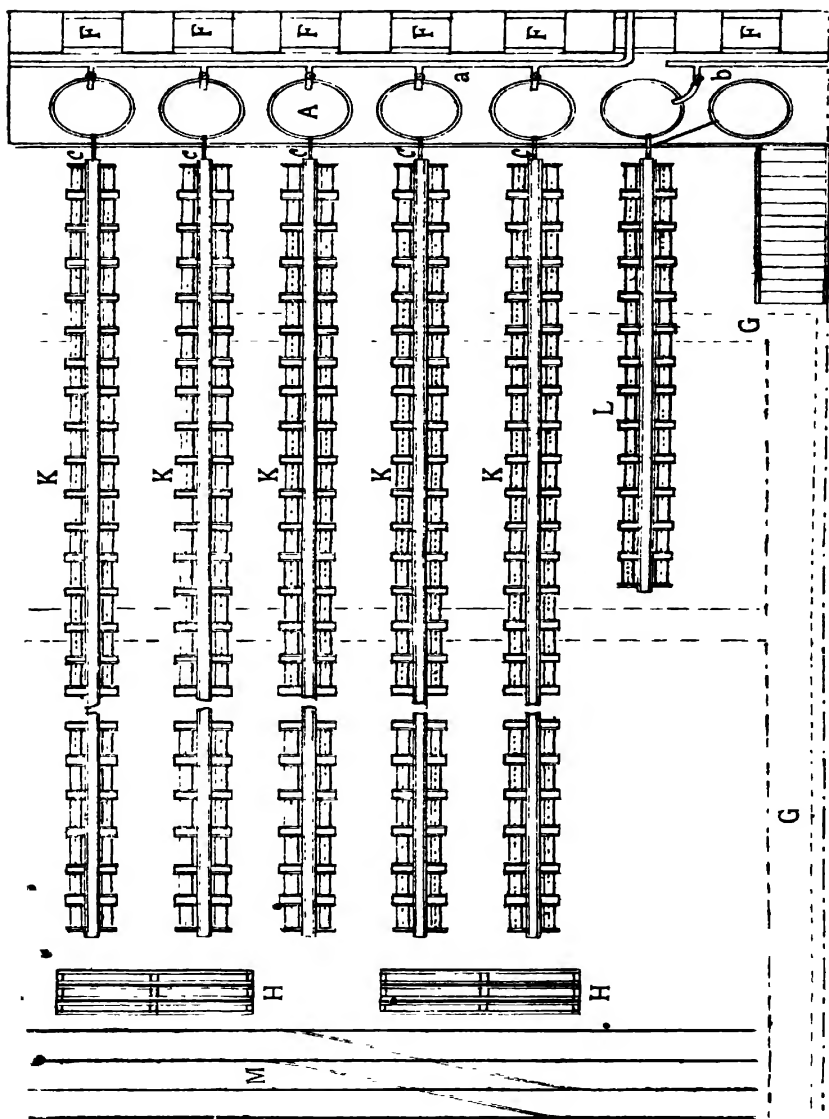
Fig. 33.

silk on these bobbins.   In Figs. 33 and 34, *c* is a bent glass
tube which conducts the liquid to two branches *c*, Fig. 36 ;
these two branch pipes extend the whole length of the banks.
From these glass branches *c*, and at equal distances apart
corresponding to the vertical rows, are further branch tubes *d*,
but of indiarubber, Figs. 35 and 36 ; the extremity of each
tube is provided with a little ebonite tap which dips into the
perforated celluloid gutters *e*.   The solution from the tanks
A, Fig. 34, reaches these gutters by the above arrangement
of pipes and tubes, one gutter being provided for each
vertical row of bobbins.   The liquid thus drops from the
several holes of each gutter on to the silk of the top bobbin I,
in each row.   Here it separates into two streams, each of
which, after having traversed half the circumference of this
bobbin I, drops on to the second bobbin II ; the liquid flows
over both sides of this bobbin in a similar manner, and so on
until every bobbin in the row has been washed.   The bobbins
of silk I, in the top horizontal row, after having been washed
in this way for six hours, are taken from the bank and are
placed in a shorter bank L, Fig. 33, where they are washed
with soap.   The bobbins in each horizontal row K are now
moved to the row above, the bottom row being thus left empty.
This row is immediately filled with a fresh set of bobbins
which the doffers bring from the last doffing of the spinning
frame.   At the end of one hour—that is to say, after each
doffing of the spinning frame—the bobbins in the bank are
raised to the next row, so that each bobbin remains for one
hour in each row from bottom to top before it is taken to the
bank L.   It is an advantage to have six perforated celluloid
gutters *e*, Fig. 35, in each vertical row, one immediately above
each bobbin, although they are not represented in the figure.
It is also an advantage to give a quarter-turn to each bobbin
when lifting it to the next row.   In several works the material
is washed in distilled water for five minutes between the
acid treatment and the operation of washing with soap.

   Below we give particulars of the most common solutions
which are used in the washing of artificial silk.   Into a stone-
ware tank C, Fig. 34, placed under the platform D, are poured
three carboys of ammonia (12 kgs., or 26·448 lbs., per carboy)
and three carboys of acetic acid (strength 80 per cent.) ; this
mixture is afterwards diluted with water until the tank C
is completely filled.   Half a litre ($\frac{1}{9}$ gal.) of the solution in
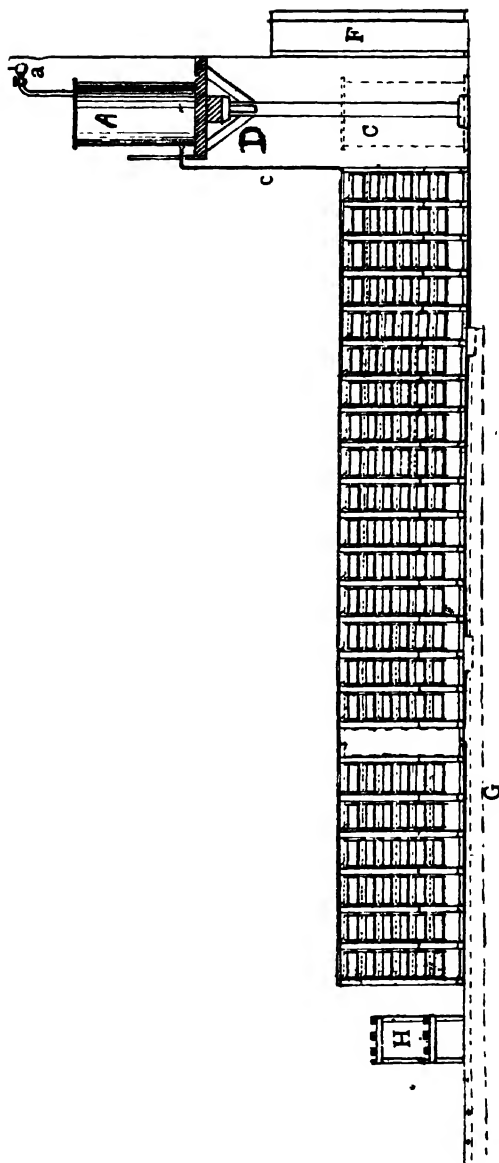
Fig. 34.

the tank C is poured into each of the five tanks A, and these tanks are then filled with water from the pipe *a*. The tanks A empty themselves in about an hour, and it is easy to calculate how long the prepared mixture in tank C will last ; for example, suppose a tank contains 1250 litres, and five litres are required every hour for the tanks A, tank C will clearly be emptied in

$$\frac{1250}{5} = 250 \text{ hours.}$$
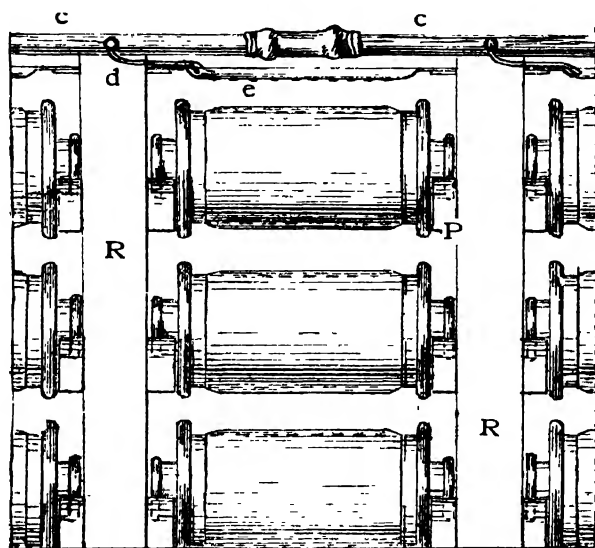
FIG. 35.

A more recent solution, and one that has given excellent results, is made up as follows : Three carboys of formic acid are poured into tank C, Fig. 34, which is then filled up with water. Three litres ($\frac{2}{3}$-gal.) of this liquid is poured into each of the tanks A, Figs. 33 and 34, which are also filled up with water. The following method is used to ascertain if the artificial silk has been sufficiently washed : 15 grms. of barium chloride are dissolved in a litre of water, and into this solution are poured a few drops of the water which has just been used for washing the bobbins in the bank ; if the silk has been sufficiently washed the barium chloride solution remains clear, but if the silk has been imperfectly washed an insoluble precipitate of barium sulphate is thrown down.

Filtration of the Water.—The purity of the water for the washing and for the soap washing of artificial silk, as explained in the last section, is of the highest importance. There are two methods of purifying water : Natural and artificial filtration. Natural filtration, which is the more perfect method, must take place on large filtering surfaces, and must be carried out as slowly as possible ; the cost, however, becomes very great. Artificial filtration lends itself better to daily requirements, but it demands a continual supervision, and when it is a question of filtering a large quantity of water, the operation can only be carried out at the expense of the quality ; indeed, in course of time the impurities in the water collect on the filter, and the filtration becomes either slow or imperfect. Moreover, the water used for washing, and that which is utilized for the preparation of the cellulose and the ammoniacal copper oxide, should contain as little lime and iron as possible, if it is desired to manufacture a lustrous thread. The works

FIG. 36.

that are obliged to use water containing calcium carbonate or iron produce a dull silk ; this can be sold only at a low price, which is seldom sufficiently remunerative.

Before a site for an artificial silk manufactory is decided upon it is of the utmost importance that an analysis of the water should be made. The water used in the manufactory of Givet is excellent, and to this fact may be ascribed the beauty of the artificial silk made in these works. Even with the best refiners it is impossible to purify water to such an
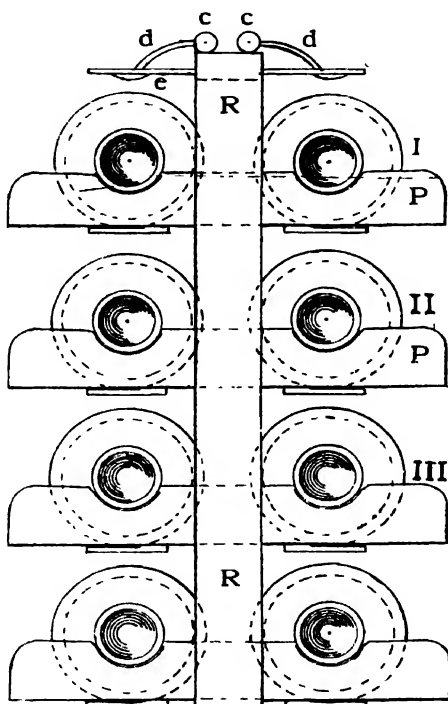
extent as to avoid the formation of precipitates—and these precipitates prevent the production of a lustrous thread. We have also stated that a thread which has been washed for six hours or more on a bobbin by the gutter system of "Glanzstoff-Fabriken" is duller than one washed for only four hours, the former one being marked or scratched, as it were, by the water.

Soap Washing.—When the bobbins of artificial silk have been washed for six hours, they are placed, as has been already stated, in a shorter bank L, Fig. 33, washed for two or three minutes in soap-suds, and then taken through the double
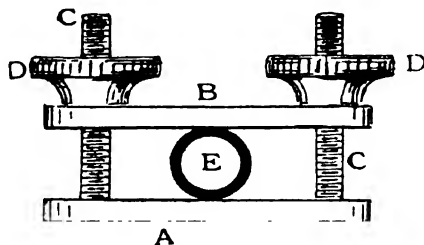
Fig. 37.

doors F, F into the dryhouse ; 5 kgs. (11·02 lbs.) of Marseilles soap, guaranteed 80 per cent. pure oil and alkali, are mixed in one of the vats B with 1250 litres (275 gals.) of condensed steam kept at 50° C. (122° F.) and delivered by pipe *b*. To this mixture are added 4 litres ($\frac{0}{10}$ gal.) of ammonia and a little borax. The whole is agitated for some time with a long bamboo cane ; and the mixture must be kept at a temperature of 50° C. (122° F.), not only during the preparation of the suds, but also during the whole of the time that the artificial silk is being washed. For such a high temperature the cellulose gutters are replaced by wooden or glass ones : it is no longer advisable to use ebonite taps, and these are advantageously replaced by plated iron clamps shown in Fig. 37, in which E is the indiarubber tube between the clamps A and B. The rate of flow of the soap-suds may be regulated at will or stopped entirely by means of the clamps A and B, the screws C, and the milled heads D. This washing with soap renders the thread more supple and slippery ; it thus facilitates, at a later stage, the winding. An increased production of 50

per cent. in the winding is obtained when this soap washing is properly carried out.   All traces of soap are removed by washing (eventually bleaching) at the end of the operations, when the yarn is in the form of hanks.

In virtue of a slight inclination of the floor, the water that has been used for washing, as well as the suds, is drained away by the grooves in the flags into the subterranean channels. The floor of the spinning room is, for the same reason, constructed with a slight inclination as shown in Figs. 20 and 21.

CHAPTER X

Drying, Humidification, and Ventilation

THE DRYHOUSES.--When the washing is completed, the bobbins are taken into the dryhouse, where they remain from fifteen to twenty hours in a strong current of air and at a temperature of 40° C. (104° F.), so that they may be dried thoroughly. In each drying room there are nearly 6000 bobbins arranged in tiers, each bobbin containing on an average 27 grms. (0·95 oz.) of artificial silk. It is clear that perfect ventilation, together with a maximum heating surface, will hasten the process of drying the artificial silk ; however, it is as well not to raise the temperature above 60° C. (140° F.), without introducing artificial moisture, for we have already seen that a temperature of 90° C. (194° F.) is sufficient to cause reddish-brown stains, which, according to Bronnert, are due to traces of copper remaining in the artificial silk, and which would volatilize. This observation, however, does not appear to be justifiable, seeing that copper volatilizes only at a much higher temperature.

The action of heat on cotton fibres, fabrics, paper, etc., is also well understood, and everyone knows that a piece of paper or a small piece of cloth is much more supple when dried in the open air, or in a room normally heated and humidified, than when dried quickly in a very hot room. Artificial silk is especially susceptible to high temperatures which rapidly impart a yellowish stain ; it must therefore be dried with great care.

The first drying especially--at which stage the silk is still in a more or less pasty condition--must be done slowly and under conditions which have been found to be most satisfactory. After the first drying, the silk may be soaked in water a number of times, and may be washed for several hours, and although it swells and loses part of its strength, it never returns to the pasty or gelatinous state which characterized it before the first drying. During the first drying, the artificial silk filaments seem to solidify and to be more closely bound together ; they are thus enabled to resist subsequent washings, and even high temperatures, without injury. After the second

and third washings the artificial silk is, at the same tempera-
ture, dried much more rapidly than after the first washing.

Fig. 38 is a microscopic enlargement of an untwisted
artificial silk thread made by the cuprammonium process.
The thread is 160's count (16 filaments more or less separated),
and it was photographed as it appeared during the winding
process. Fig. 39 is a similar microscopic enlargement of a
thread of artificial silk made by the cuprammonium process
and precipitated by sulphuric acid. This thread was immersed
for one hour in ordinary water. The filaments filled with water

Fig. 38.

decrease in length, increase by 60 per cent. in diameter, and
lose two-thirds of their strength.

The green stains that are sometimes observed after drying
proceed from a fault in the washing. It is a well-known fact
that the artificial silk thread on the bobbins in the upper rows
usually dries more quickly than that on the bobbins in the
lower rows. Seeing that this is the case, and also for the
purpose of preventing loss of time and heat, it is a general
practice to allow the steam to circulate in the heating pipes
during the time that the drying room is being restocked with
washed bobbins—the dried bobbins are removed by com-
mencing at the top row and working downwards, while the

refilling commences at the bottom row and proceeds upwards ;
in this way the bobbins in each row are exposed to the heat
for a longer time than are those in a higher row, and have,
consequently, more time to dry. It is also an advantage not
to allow these rooms to cool completely, and it is advisable to
have a door at each end of the room so that the washed bobbins
may be taken out of one door, and those from the spinning
room brought in at the other. It is also necessary to see
here, as well as in the spinning and washing rooms, that the
soaked artificial silk on the bobbins does not come in contact

Fig. 39.

with any other object—not even to be touched with the
hand—during the transit from one department to another,
for the least blow or shock to the silk leaves its impression on
several layers ; it cannot, therefore, be wound after drying,
and can only be used for waste. In order to remove spoilt
silk easily from the glass bobbin it is a good plan to divide it
with a knife into parts.

Since those persons ordinarily employed for the transit of the
bobbins are from 16 to 20 years of age, it is advisable that they
should be superintended by a strict overseer, for with 100
damaged bobbins per day—which may easily happen under
imperfect supervision in an establishment where more than

5000 bobbins are filled with silk in eleven hours—the loss is considerable. Thus, 100 bobbins, each containing 27 grms., represent 2·700 kgs. (5·95 lbs.) of silk, and if the material is worth 15 francs per kilogramme (5s. 4¾d. per lb.) the loss per day would be represented by 40 frs. 50 c. (£1 12s. 2d.). But in many cases the glass bobbin is broken at the same time that the silk is damaged, and under the above circumstances we can estimate without exaggeration that in one day, out of 12,000 bobbins which circulate in the various departments, about 30 will be slightly damaged, and 50 to 80 broken. In order to reduce the number of breakages to a minimum, and to dispense with hand labour as far as possible, the Glanzstoff factory convey the bobbins to and from the different departments by means of an overhead trolley.

Humidification.—When the silk is perfectly dry, the bobbins are taken out of the drying room and kept for four or five hours in a special room to be humidified ; this process facilitates the operation of winding. A general rule for humidification cannot be well established, seeing that there are as many different opinions, and as many different types of installations, as there are directors ; moreover, artificial humidification is influenced by the surrounding atmosphere, and varies considerably according as the air is more or less saturated with water vapour. An advantageous system for this industry would, in our opinion, be somewhat as follows : On leaving the dryhouse, the bobbins would be placed in a separate building of brick, raised slightly, 2 m. 20 (7 ft. 3 ins.) at most, from the ordinary level, and with a slightly inclined concrete floor, so that if necessary cold water could flow between the superposed bobbins. A series of windows and chimneys would establish a current of air that would be regulated according to the outside temperature. At the end of a certain time an intelligent overseer would humidify the silk to the most advantageous condition for winding. A ready means of ascertaining whether or not the silk possesses the necessary amount of moisture is to touch the bobbins ; a hygrometer, however, is here an absolutely indispensable instrument.

Before installing a system of humidification, it is wise to study thoroughly the place and its surroundings, and afterwards to choose a high-class humidifying plant. We may mention that a humidifying apparatus should be installed,

not only in the humidifying room, but also in the winding room and in the twisting room ; for, in addition to improving the condition of the silk and increasing the production, its use is to be recommended from a hygienic point of view.   In cotton spinning this beneficial hygrometric influence has been known for many years, but it was determined only after numerous observations.   It is not surprising that artificial silk is also prepared most satisfactorily under well-chosen conditions of temperature and humidity, and that its physical properties may be sensibly modified by the presence or absence of hygroscopic moisture.

The humidification of the bobbins before reeling has been replaced in different works by steam jet humidification.   To this end the bobbins are placed in a closed cage in which steam circulates for ten minutes.   When caustic soda is used instead of sulphuric acid for precipitation in the spinning room, this humidification is unnecessary.   The thread is sufficiently strong after the first drying to be reeled in a damp or humid state, and it is sufficient to plunge the bobbins into ordinary water before reeling the silk from them.   An addition of weak acetic acid to the water, however, is advantageous.

In connection with the use of caustic soda baths, it has been found impossible to dispense with glass bobbins and to use in their place bobbins made of special metal.   In addition to the above advantage, artificial silk spun with the aid of caustic soda in the cuprammonium process is, perhaps, the strongest of all artificial silk threads, and by this process it is even possible and practicable to spin 30 to 40 denier silk strong enough to be woven.

An excellent measure to take with the aim of lowering the temperature of the ground floor during hot seasons is to whiten the roofs of the works with whitewash.   The temperature of the rooms in July and August may be lowered from 4° to 5° C. (7·2° to 9° F.) by this means.   A single application suffices for the hot season ; the quicklime is converted into calcium carbonate, which, by means of alum, adheres to the tiles and windows of the roof.

Ventilation.—The ventilation of the workshops is now considered most essential for regular and productive work. The air vitiated by deleterious vapours must be withdrawn, from the rooms.   There is not only a well-known economic reason for this process, but also a superior motive—that of

providing hygienic conditions for the workmen. The first essential consideration of a ventilator outside excellent mechanical construction, is that of obtaining the maximum displacement of air with a minimum motive power ; the second is that of performing the work without causing draughts. Ventilation combined with humidification produces remarkable results, and this type of combination is exemplified in the industries where noxious vapours or gases are created—gases which are harmful to manufacture or to health.

The improvement in the conditions for the processes of manufacture is naturally followed by improved hygienic conditions. The artificial regulation of the hygrometric state constitutes an excellent measure for the purification of the air ; the heavy particles fall to the ground, and the workman, in comparatively healthy surroundings, performs his task with an attentive regularity that would not otherwise be possible. The combined operations of ventilation and humidification may be advantageously carried out by means of any of the well-known systems invented for the purpose. The apparatus invented by Munk (Kestner system) clears from particles and cools 40,000 cubic metres of air (approximately 1,400,000 cu. ft.) per hour. The humidification of the air, which may reach 70 per cent., is perfectly uniform, and is effected without deposition of drops.

The Glanzstoff-Fabriken recover the ammonia, which is liberated during the spinning by means of powerful exhausters.

When caustic soda baths are used instead of sulphuric acid baths in the spinning room the ventilation must be very energetic, for the liberation of ammonia is excessive. Foltzer recovers the ammonia at the mixers and also at the alkaline baths. In this way a large quantity of ammonia is recovered which can either be used again in the manufacturing process or transformed into ammonium sulphate. The introduction of apparatus for recovering the ammonia at the mixers and at the spinning frames in the cuprammonium process effects economy, and similar apparatus might, perhaps with advantage, be attempted in the Viscose and other processes, especially as the recovery process is very simple and rapid, and the silk strong even when the temperature of the water or the dye liquor reaches 80° to 100° C. (176° to 212° F.).

CHAPTER XI

Winding, Twisting, Reeling, and Counting

THE operations of winding, twisting, and reeling being very similar to those practised for ordinary silk yarns will be only briefly described.

The thread, which comes from the spinning room, is composed of a certain number of smaller threads or filaments, which are parallel to each other and in juxtaposition. The operation of twisting draws these individual threads closer to each other, thus making a more compact structure. The large glass bobbins A, Figs. 40 and 41, although quite satisfactory for the spinning process, are not quite suitable for the process of twisting, hence the threads are wound from these large bobbins on to much smaller bobbins B, ready for the twisting frame.

The machine, which is used for this preparatory winding, is composed of a wooden table E, at equal distances on which are placed the glass bobbins A, A. The thread K passes over a wooden guide pulley D fixed to a beam which extends the full length of the machine, and which carries the necessary number of guide pulleys. The thread guides H are fixed to a rod G, which is supported by and moves on anti-friction rollers F. The rod G moves in the ordinary way from side to side of the bobbin B so as to lay the silk evenly on the bobbin. Bobbin B is driven by frictional contact with wheel C, which is mounted on a spindle and rotates as indicated by the arrow. An enlarged view of bobbin B is shown in Fig. 42, as well as the method of securing it to the spindle A by means of the wing-nut C.

The glass cylinders A, Fig. 41, instead of being placed as shown, may be suspended about point D by brackets supported by the beam. The glass bobbins are arranged to be perpendicularly above the bobbins B ; the winding is then performed more easily, and the threads, besides receiving less drag, have a tendency to come off the bobbins by virtue of their own weight. We have adopted this arrangement with success, the production being increased and the breakages less frequent.

When the bobbins B are filled with the yarn they are placed

on a bobbin board, Figs. 43 and 44, and then they are taken
to the twisting department. The bobbin boards usually hold
twenty-one bobbins. The twenty-one empty bobbins and
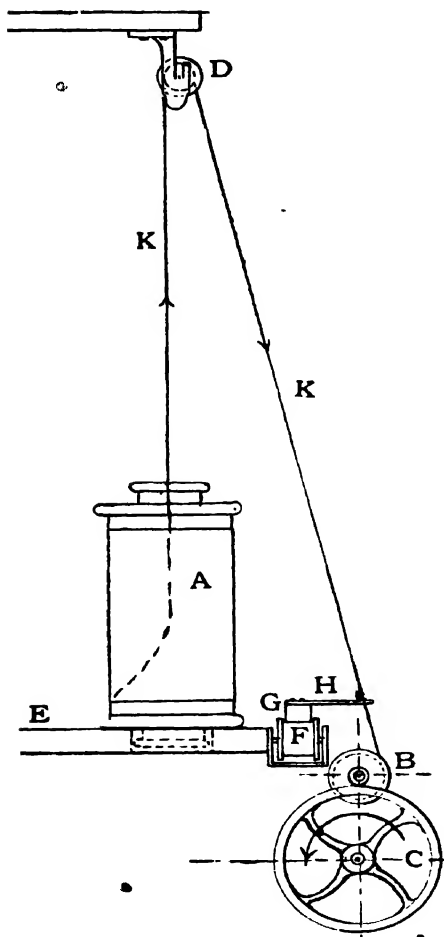
Fig. 40.
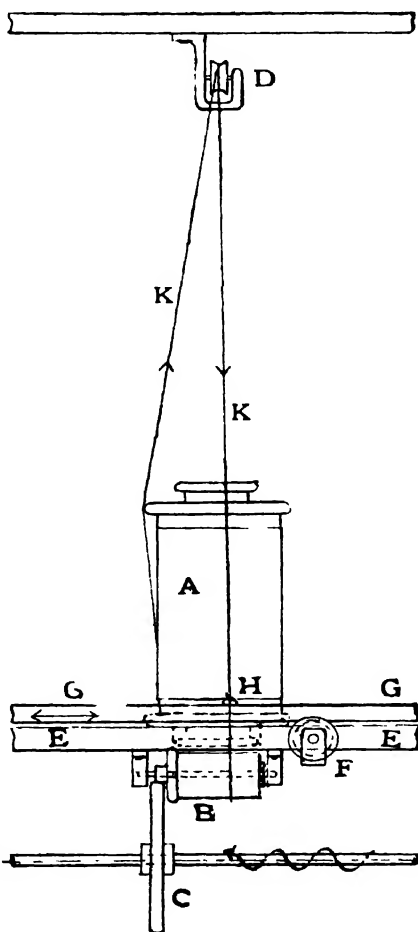
Fig. 41.

board are weighed carefully, and the same again weighed
when the bobbins are filled with silk ; each workman thus
records the net weight of silk which passes through his hands.
There are from fifty-five to sixty bobbins in the twisting

machine, and each workman attends to five or six bobbins, from which he will take off an average weight of 3 kgs. (6·612 lbs.) per day. The rate of pay depends, naturally, upon the count of the silk. Thus, in 1909 the rates were—

For 100's to 120's count, the rate is 0 fr. 80 per kilog. (3·4d. per lb.)
  ,,   120's ,, 160's ,,   ,,   0 fr. 62   ,,   (2·7d. ,,)
  ,,   160's ,, 200's ,,   ,,   0 fr. 50   ,,   (2·2d. ,,)

In the twisting frame the wooden bobbins B, Figs. 45 and 46, which come from the winding frame, are mounted on spindles A, driven by frictional contact with belt C from pulley D. The twisted thread is wound upon another wooden bobbin F, which is driven by frictional contact with the drum E. After leaving the bobbin B, the thread passes through the fixed thread guide H, and then through the second thread guide G, which moves laterally to and fro between the edges of the bobbin F. The drums E are fixed on shaft O, which receives its motion from the shaft carrying pulley D by means of wheels K and L, shaft N, and bevel wheels M. Provision is made for moving the top bevel wheel M along the shaft O, so that wheel L may be moved into gear with any of the wheels K, and thus vary the speed of the drums E according to requirements.
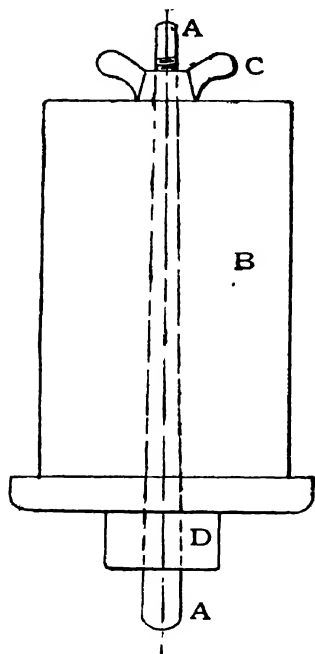
FIG. 42.

Silk Throwing or Reeling.—This process consists of winding the artificial silk threads into the form of hanks, and is almost identical with that used for natural silk. The machines for both kinds of silk being of the same construction, they need not be described here. Readers who wish to study this branch will find detailed particulars of the operation in one or other of the books that deal with natural silk. We must state, however, that in the processes of winding, twisting and reeling, the workmen must be careful not to tie together

threads of different counts or sizes. With a little practice, the operatives can judge the sizes by the eye without actually testing them.
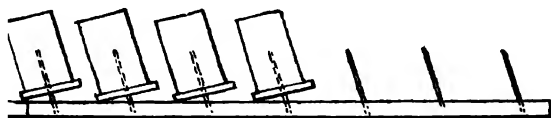
Fig. 43.
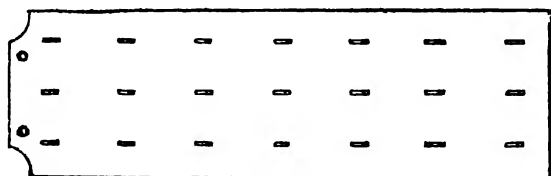
Fig. 44.

The silk yarn, after being thrown or reeled into hanks, is placed in a washing machine and washed with dilute acetic acid (1 part acid to 500 parts water). This machine is of the same type as that used for the washing of natural silk, and contains porcelain rollers which turn alternately in both directions.

A more recent method consists of washing the finished silk in oxalic acid (200 grms. for 500 litres; 0·44 lb. for 110 gals.), which produces a much whiter silk than if washed with acetic acid. After having been washed, the hanks are dried, and then placed on pegs from which the workmen sort the threads in order to remove the knots and nap. The silk is then numbered according to count, packed up, and despatched to the buyers.

The Count, Size, or Number of the Yarn.— The count of artificial silk is the relation between its length and a fixed weight. It therefore indicates the degree or fineness of the thread. The count or size of a yarn may, however, be in terms of a fixed length and a varying weight.
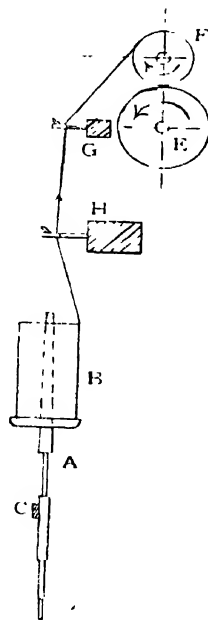
Fig. 45.

For natural silk the French unit of length is 400 ells, or 476 metres (520·56 yds.), and the weight of this length in deniers indicates the count; 1 denier = 0·0532 grm. Thus the count of the thread is the weight in deniers of 400 ells, or 476 metres (520·56 yds.). Since 1 denier = 0·0532 gr. or 0·001875 oz., there are 533⅓ deniers per oz., or 8533⅓ deniers per lb. The method of counting is identical with that for
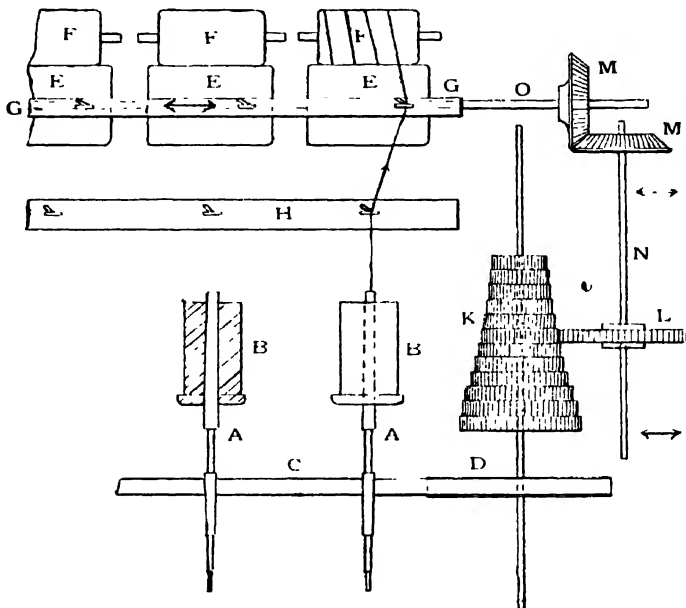
FIG. 46.

raw silk, but directly opposed to that of spun silk and cotton. The methods of conversion are as under—

$$\frac{520 \text{ yds.} \times 8533\frac{1}{3} \text{ deniers}}{\text{denier count} \times 840 \text{ yds.}} = \text{cotton or spun silk count.}$$

$$\frac{520 \text{ yds.} \times 8533\frac{1}{3} \text{ deniers}}{\text{cotton or spun silk count} \times 840 \text{ yds.}} = \text{denier count.}$$

Thus, 40° cotton or spun silk, when converted to artificial silk count is as under—

$$\frac{520 \times 8533\frac{1}{3}}{40 \times 840} = 132 \text{ denier.}$$

or, more simply, $\dfrac{5280}{40} = 132$ denier, since

cotton count $\times$ artificial silk count $= 5280.$

For artificial silk the individual filament is equal to about 10 deniers, and in general a group of 12 to 14 filaments forms the ordinary counts of 120 to 140 deniers. It is usual, however, to try to form the fine numbers by grouping a large number of individual filaments ; thus, the individual filament is made as fine as possible, and consequently the finished thread possesses great strength, and is very supple.

La Société Bemberg à Barmen, which carries on the work under Thiele's patents—a process of drawing the thread before its complete precipitation—has also achieved good results by the above methods. (In England these processes have become the property of the United Cellulo Silk Spinners, Ltd., London and Great Yarmouth.)[1] Mr. W. P. Dreaper mentions in his report that he has received samples of artificial silk of 25 deniers which contain 60 fibres or individual filaments, and which have a breaking weight of 58·5 grms., or about 2·3 grms. per denier. Its resistance to breaking is therefore as great as that of many natural silk threads. The above figures show clearly the progress which the artificial silk industry made during a period of ten years, for in 1900 La Société Industrielle de Mulhouse report on this question that the best artificial silk threads of 100 deniers (10 filaments) had a breaking weight of 120 grms., and 8 to 10 per cent. elasticity. For many years attempts have been made to introduce the metric system, and so obtain uniformity in relation to the counting of silk yarns, and in general to all textile materials, but the attempts have not been successful.

[1] Artificial silk is made on the same principle by Brysilka, Ltd., Apperley Bridge, Yorkshire.—*Transr.*

CHAPTER XII
Waste

First of all there is the waste caused in the spinning department when the solution escapes as a result of a leakage due to a defective valve, the bursting of a glass pipe, the splitting of an indiarubber tube, or the breaking of a distributor. These accidents are quite inevitable, and the loss of solution must be prevented as far as possible by a prompt replacement of the broken glass pipes or the split indiarubber tubes by new ones. The waste caused by these accidents added to that made by the piecers when tying or joining the broken threads is considerable, and may be as much as 20 per cent. of the production. The waste is removed every day from trough d, Fig. 23 (p. 55), and deposited in a wooden tub or box of about 100 c. ft. capacity, situated outside the building. This accumulation of waste is sufficient to fill about three-quarters of the tub in fifteen days ; the remaining quarter is then filled up with water, and the whole pressed for some time. Afterwards the water is allowed to run out through a tap at the bottom of the tub. This operation is repeated until the water which escapes is almost clear, for this water contains ammoniacal copper oxide which is recovered.

In addition to the above waste there is also the winding waste, which is of three kinds—

(1) The ordinary waste that occurs whenever a thread breaks, and which represents the defective portions of that thread ; each faulty part must be removed before the ends are joined.

(2) The waste caused by the cut silk—that is, the material which is cut from the damaged cylinders"; also the silk that contains thick parts, and entangled threads, which prevent quick and satisfactory winding.

(3) Greasy waste.

Then there is the waste caused in twisting ; this, however, is not considerable.

The following figures give an idea of the waste in the different sections ; they represent actual observations made in April and May, 1902 and 1903, and are taken from the first edition

(French) of this work. Improvements in the method of
dealing with the prevention of waste have since been effected,
and therefore better results are now obtained—

						April.		May.
Waste in winding	.	.	.	.	per cent.	5·00 kgs.	.	6·00 kgs.
,, cut from cylinders	.	.	.	,,		4·00 ,,	.	4·80 ,,
,, in twisting	.	.	.	.	,,	2·00 ,,	.	2·20 ,,
Greasy waste	.	.	.	.	.	,,	4·00 ,,	.	3·00 ,,
Total	.	.	.	.	,,	15·00 kgs.	.	16·00 kgs.
Waste in spinning	.	.	.	.	,,	18·00 ,,	.	13·00 ,,
Silk of proper count (120 to 180)	.		,,	59·00 ,,	.	63·50 ,,		
Silk of wrong count, too heavy or too								
irregular	.	.	.	.	.	,,	8·00 ,,	.	7·50 ,,

100·00 kgs. . 100·00 kgs.

Waste Caused by the Stoppage of the Spinning Process.—
When it is desired to stop the process of spinning, the
capillary tubes are taken out of the sulphuric acid trough
d, Fig. 23, an operation that may be quickly done by removing
the rubber tubes which connect the capillary tubes to the
distributors *f*, and the latter to the glass taps *i*. When the
machine is stopped, each capillary plate N, Fig. 24, is covered
with a small indiarubber tube or hood about 5 mm. long.
This hood is filled with the solution before the glass tap *i* is
closed. In this manner the solution, instead of losing its
fluidity and becoming viscous in the narrow neck of the
capillary tube through contact with the air, thickens in the
indiarubber extension or hood. When the spinning frame is
again ready for starting, the indiarubber hoods are removed,
the glass taps *i*, Fig. 23, are opened, the capillary tubes are
placed in position in the sulphuric acid bath *d*, and the solution
under pressure issues from the capillary tubes, and floats, in
the form of threads, on the surface of the acid bath. A
similar effect to that obtained by the indiarubber hoods
results from plunging the capillary tubes into the water in
trough *c* at the moment when the machine is stopped. The
stoppage of a frame always causes a loss of time, and also
creates a certain amount of waste ; suppose that a quarter
of an hour is lost at each stoppage, and that the average
production is 27 grms. (415·8 grains) per hour from each
distributor, then there would be a loss of—

$$\frac{27}{4} \text{ grms.} \times \text{ number of distributors ;}$$

or 6¼ grms. (96·25 grains) per distributor per hour.

It is for the purpose of obviating this disadvantage that the machines in artificial silk factories run continuously, night and day, from Monday morning to Saturday night. Two, and sometimes three, shifts of workmen attend successively for twelve or eight hours each. Without advising night work, which is injurious to the health of the workman, and which results in the production of inferior silk, we must say that the practice of employing three shifts of workmen is much better than two shifts, seeing that many of the workmen, instead of resting during the day, walk about or devote their time to other pursuits, and when night comes they are not in a fit state for following an occupation that demands care and attention ; it is better, therefore, to have three sets of workmen, for then each workman has sixteen free hours ; this period leaves him sufficient time for sleep as well as for recreation. But the arrangement of three shifts of eight hours each is only practicable for those workmen who, in addition to the work provided for them in the factory, have facilities for carrying on some supplementary work in their own homes. The factory wage for eight hours is not sufficient for their wants, and if some supplementary work is not obtainable, a higher rate of wages must be paid for their time at the factory. As regards meal times, the operatives of each shift relieve each other, so that one-third take their meals from, say, 11 to 12, the next third from 12 to 1, and the remainder from 1 to 2. During these three hours one-third of the workers are, therefore, absent, and the remaining two-thirds take charge of the whole of the work. In order to carry on the work efficiently during these periods, it is usual for some of the operatives from the washhouse, dryhouse, and repair shop to help, for each person in these departments may, if so disposed, find liberty to assist for half an hour or more.

Utilization of Artificial Silk Waste.—When the manufacture of artificial silk was first commenced, the percentage of waste was very considerable, and some difficulty was experienced in recovering the secondary products ; at this time, however, by way of compensation, a higher price was obtained for the silk, so that the selling price of the waste was of little importance. But in the year 1909, when the price of good silk had fallen more than 15 francs per kilogramme (5s. 4¾d. per lb.), and when competition had become so keen

a few francs' worth more or less per kilogramme of waste had certainly an influence on the net cost, and this could not be neglected. The waste silk cut from bobbins, of which we have just spoken, was readily sold for the manufacture of wigs for theatrical purposes, and also for the manufacture of children's toys ; but the price that was obtained was insignificant. On the other hand, the silk which had been stained during the process of manufacture was of practically no value, for the cost of scouring, cleaning, or bleaching would have been so high as to leave only a small margin for profit after the cleaned waste had been sold. The entangled and damaged hanks of silk were sold as well to customers in a small way ; these customers could afford to pay several francs per kilogramme for the material, which they rewound on to bobbins or else into hanks. The high price that was obtained for this reprepared silk left them a relatively large profit in spite of the expense incurred by handwork. Some manufacturers of artificial silk did this rewinding themselves, then dyed the silk in dark shades, and sold it off as a second quality. But all this has now changed, since there is no longer, even for good silk, more than two to three francs between the net cost and the selling price. Under these conditions the chief aim of the artificial silk manufacturers is to reduce, by all possible means, the production of merchandise of second and third rate quality. On the other hand, new outlets have been found for waste silk, and the manufacturers still wind the slightly entangled hanks to be used up as silk yarn ; but all that which is defective or badly entangled is cut from the bobbins and reels and put on one side to be sold as waste. This waste is then used, mixed with other threads, for certain classes of trimming, such as tassels, etc.

By the German Patent 194506 it has been shown how to manufacture felted cellulose from cut waste ; we shall speak of this in the chapter that deals with similar products.

Fancy pellicles may be made with a solution of cellulose and a mixture of variously coloured filaments. Other branches of the textile industry have commenced to utilize this waste silk with more or less success. Thus some spinners of cotton waste, and also some spinners of wool and ramie, especially in Austria and Germany, mix the silk waste in greater or less quantities before spinning with cotton, wool, or ramie, and obtain by this means a lustrous effect in the finished

yarns. In order to obtain different effects, dyed cotton or dyed wool may be mixed with bleached artificial silk. By this recent departure artificial silk waste will perhaps obtain a considerable outlet. Trials have also been made to spin the waste alone, after it had been cut up into different lengths ; but we believe the results have not been satisfactory[1] ; the artificial silk threads or filaments do not appear to be able to withstand the friction in the processes of drawing and twisting to which cotton and wool are subjected. The small degree of success that has attended these trials is due perhaps partly to the deficient flexibility of the artificial silk, and partly to the different chemical processes which are employed in its manufacture. No practical results have attended the efforts to spin artificial silk waste in a moist state by lubricating it slightly with soapy water or with a mixture of oil and water. However, we must mention that it is now possible to spin thick threads from silk waste—these are called *chappe de soie artificielle*. This thread resembles in some measure a woollen one, but it is not so agreeable to the touch ; it is very lustrous, and the ends of the silk, which cannot be made to lie closely to the body of the thread by twisting, stand out like bristles. Shawls, bonnets for children, and similar articles termed *chappe de soie artificielle*, have been made from such yarns.

We may also mention a process of the Glanzstoff Fabriken (British Patent 15,700, 1910) by which it is possible to re-dissolve the artificial silk waste in warm concentrated formic acid, and to re-spin the solution. We are not aware that this process is applied industrially, but we shall have occasion to speak of it later.

[1] This process is now a practical proposition.—*Transr.*

CHAPTER XIII

Viscose Artificial Silk Threads and Other Products

In 1892 Messrs. Cross and Bevan patented a process for obtaining a remarkable compound of cellulose—the thio-carbonate of cellulose. Much was expected from this product at the time of its discovery, not only from an industrial and financial point of view, but also from a scientific point of view, as it was thought that it might possibly lead to the discovery of the true constitution of cellulose. The thio-carbonate of cellulose, or viscoid, as it has been named by the inventors, is obtained by treating an alkali-cellulose with carbon disulphide at the ordinary temperature.

$$\mathrm{XONa} + \mathrm{CS_2} = \mathrm{CS} \underset{\mathrm{SNa}}{\overset{\mathrm{OX}}{\diagdown}}$$
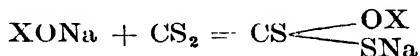
The resulting compound is therefore an alkali-cellulose-xanthate. Hydrocellulose manufactured according to Girard's method may be used instead of pure cellulose, in which case the amount of caustic soda and of carbon disulphide would be reduced by one-half.

At a conference on artificial silks held at Nancy, M. Haller stated that the best results are obtained when the cotton is treated at a predetermined temperature with an excess of a 15 per cent. solution of NaOH ; then to press it until it held three times its weight of solution. It should then be placed in a ground stoppered bottle with 40 per cent. of its weight of carbon disulphide. After remaining in this state for about three hours at the ordinary temperature, sufficient water is added to cover the substance ; the whole is then left for several hours so that the hydration may be completed. By agitating the substance a homogeneous liquid is obtained that may be diluted according to requirements.

In practice it is usual to make the solutions with 10 per cent. of cellulose ; on account of the great viscosity of these cellulose solutions, it is difficult to prepare a solution which contains more than 20 per cent. of cellulose. Solutions prepared as

above have a yellow colour, due to secondary products of reaction (trithiocarbonates). The characteristic properties of the xanthates of cellulose are—

(1) *Spontaneous Decomposition.*—When the decomposition takes place in aqueous solution of a concentration greater than 1 per cent. of cellulose, a jelly or coagulum is formed.

(2) *Coagulation by Heat.*—The solution evaporated at low temperatures yields a solid which is quite soluble in water. If the process is carried out at a temperature between 70° and 80° C. (158° and 176° F.), the coagulation or decomposition is very rapid, and if the solution be then dried at this temperature thin films are obtained, and these adhere strongly to the surface upon which they are dried. The films may, however be detached from the surface by water, which removes the secondary products of the reaction. There remains a homogeneous, transparent and colourless film, which is very flexible, but which hardens somewhat in drying, although it retains a high degree of elasticity.

The cellulose regenerated from the thiocarbonate differs from the original cellulose in the following points—

(1) It contains 3 to 4 per cent. more hygroscopic moisture or water of condition—9 to 10·5 per cent. in all.

(2) Its empirical formula is $4C_6H_{10}O_5.H_2O$.

(3) Its general properties are for the most part identical with those of the original cellulose ; the OH groups, however, react more readily. It is acetylated by simply boiling with the acetic anhydride, whereas a temperature of 180° C. (356° F.) is required for the acetylation of ordinary cellulose. It has, in addition, a greater affinity for colouring matters, and combines in greater proportion with soluble bases.

The Viscose and Despeissis (Glanzstoff) silks belong to the class of ordinary hydrated celluloses, such as mercerized cotton. These celluloses can scarcely be distinguished, indeed, from the point of view of their reducing power, from cotton cellulose (there are traces of copper in the Despeissis threads) ; nevertheless, there exists a marked difference in regard to the degree of hydration between mercerized cellulose and the artificial silks of Viscose and Despeissis. On the other hand, as has been well stated by the chemist Beltzer, Viscose and Despeissis silks digest, gelatinize, and redissolve for the most part when they are treated with caustic mercerizing lyes, whereas cotton or mercerized cellulose remains insoluble.

Application of Viscose in the Manufacture of Viscose Silk.—
Stéarn, one of the inventors of electric light globes,
in conjunction with Cross, tried first to produce filaments
from viscose which would be suitable for electric light globes ;
the attempt being successful, these chemists faced the more
difficult problem of producing threads of all sizes.   By forcing
the viscose through capillary tubes into a 17 to 20 per cent.
solution of ammonium chloride it was found possible to
obtain threads as fine as desired, and absolutely regular in
thickness.   The greater part of the thiocarbonate of sodium
cellulose is decomposed and the cellulose separated.   The
decomposition is completed, and the last traces of secondary
products are removed by passing the threads successively
through baths containing freshly prepared solutions of warm
ammonium chloride, carbonate of soda, and hydrochloric acid,
and finally by rinsing them thoroughly in water.   Tests of
the strength of spun viscose in comparison with that of natural
silk, and of different artificial silks, have been made in Sweden
by Messrs. Strehlenert and Westergenen (Société Chimique de
Stockholm at the meeting of 21st November, 1891).   We give
the results of these tests in the subjoined table—

DESCRIPTION.	Breaking Load in Kilogrammes for Threads 1 mm. diameter.	
	Dry Thread.	Moist Thread.
Natural Silk { Unlustred silk	53·2	46·7
Raw silk (French)	50·4	40·9
French silk, boiled and lustred	25·5	13·6
,, dyed red and loaded	20·0	15·6
,, dyed blue-black and loaded 110%	12·1	8·0
,, dyed black and loaded 140%	7·9	7·3
,, dyed black and loaded 500%	2·2	—
Silk from Collodion { Undyed Chardonnet	14·7	1·7
,, Lehner	17·1	4·3
,, Strehenert	15·9	4·3
Pauly or Glanzstoff silk (ammoniacal copper process, and precipitated with sulphuric acid)	19·1	3·2
Viscose silk (Cross and Stéarn)	11·4	3·5
New Viscose silk (Cross and Stéarn)	21·5	—
Cotton thread	11·5	18·6

- The viscose threads dye well, withstand boiling in alkaline
lyes, resist the action of chlorine, and have a brilliant lustre

which is comparable with that of other artificial silks. Nevertheless, the product differs from the silks made from nitrocellulose in that it is easily turned slightly yellow ; this is probably due to the fact that it still contains traces of sulphur products, but the dyed material is quite equal in lustre to Chardonnet silk or to Pauly silk. The new Viscose silk, however, is perfectly white. In virtue of all these good qualities, and also of its low price relatively to that of similar products, it would appear that a great future[1] is reserved for Viscose silk.

As we can depend upon all the tests in the above table, it follows that all artificial silk products when wet lose a considerable part of their tensile strength—one of the most essential qualities of a textile fibre. Consequently, artificial silk threads can replace threads of natural silk only in particular cases—as, for example, in the manufacture of hangings, lacework, trimmings, etc. ; in short, only in those fabrics or textures which are not likely to be exposed to much moisture.[2] However, this defect in the material is being gradually overcome, and the loss of strength in artificial silk when wet is now very slight, and in the near future may be perhaps prevented altogether. In 1900 the Glanzstoff Fabriken indicated a loss of 77 per cent. for artificial silk in the wet condition ; the tests made during the first half of 1910 at Manchester, and supplied in a report by Mr. W. P. Dreaper, give only a loss of 56 per cent. for artificial silk made from nitro-cellulose, and 66 per cent. for the lustre silk obtained by the cuprammonium process.

The Despeissis silk has made fresh progress during the last few years, especially since the Glanzstoff Fabriken, the Hanover Kunstseide Fabriken, and others, commenced to use alkalies as precipitating liquids during the process of spinning as suggested by Wurtz (*Dictionnaire de Chimie*). It had indeed been known for a considerable time that artificial silk could be more quickly precipitated with this liquid, and that the products were more resistant to water ; but the industrial application of the lye of soda or potassium as a precipitating liquid is relatively recent.

Viscose is manufactured especially by the following firms : La Société française de la Viscose à Paris ; La Société générale de soie artificielle par le procédé Viscose à Bruxelles ; La Viscose du prince de Donnersmarck à Sydowasue près Stettin ;

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[1] This prediction has been fully realized.—*Trs*.
[2] *See* Celanese or celluloso acetate silk.

La Viscose italienne à Turin ; La Société suisse de la Viscose à Emmenbrucke près Lucerne.[1]   We are pleased to be able to state that after trials extending over many years the Viscose artificial silk manufacturers are able to produce the silk in quantity ; but we also think it our duty to say that those who manufacture by the Chardonnet process seem no longer to have full confidence in that system, and convert their material to work it according to the cuprammonium process, or to manufacture from it a derivative of Viscose.   The factory of Tubize, Belgium, and others, which are fortunate in respect to excellent local conditions, need not, however, be afraid of their system being supplanted for some time, more especially as the Chardonnet silk is always in great demand, and resembles natural silk perhaps more closely than does artificial silk made by any other process.   La Société française de la Viscose has disclosed some interesting apparatus and processes —

(1) To remove the air contained in the spinning solutions by creating a vacuum in a conical reservoir in which a steel cone rotates.   The solution is led into the reservoir by a pipe, and in such a way that it is evenly distributed on the walls of the cone ; from this it flows away and the air bubbles are removed by a suction pump which creates the vacuum.

(2) A capillary tube with multiple orifices for imparting twist during the spinning process.

(3) An accurate valve which provides means for regulating the flow of the solution in the capillary tubes.

(4) A spinning machine arranged as follows : The filaments that emerge from the capillary tubes are wound in turn on two little reels mounted side by side where the glass bobbin F, Figs. 23 and 22, appears in the older method.   The threads pass on to the first reel of each pair until each contains a hank of 1000 metres (1094 yds.) ; then all the thread guides move laterally until they are opposite the second reel of each pair, which are at this instant started by means of a friction bowl ; while at the same moment the other reels, which have just been filled with silk, are put out of motion.   The process is then repeated.

Another remarkable process is that of the Viscose of Stettin : The silk which comes from the capillary tube is wound in an

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[1] This continental list could be augmented considerably, because in English-speaking countries, Messrs. Courtaulds, Ltd., have extensive works.

untwisted state on to small bobbins. These bobbins are then taken to the twisting department, where the thread, loaded with chemical products, is wound and twisted in one operation, and then made up into hanks of 1000 metres (1094 yds.). The little bobbins A, Fig. 47, are mounted on a spindle B which is driven by cylinder C by means of a belt or band D. The band D passes round whorl E, and is kept horizontal by guide cylinder F. The thread G is withdrawn from bobbin
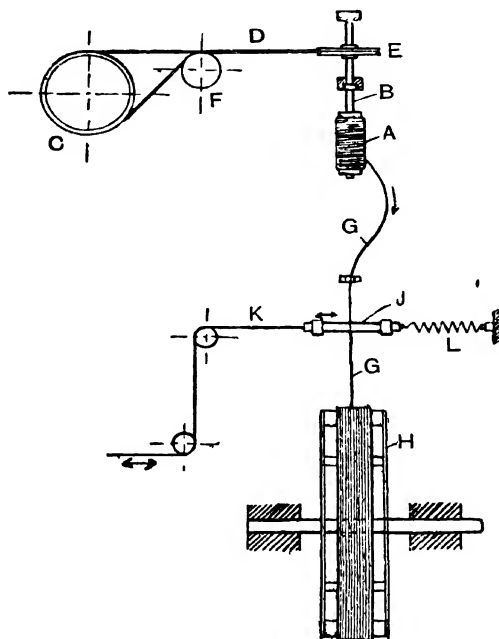
FIG. 47.

A, and is wound on reel H, during which time the spindle B is rotated at the speed necessary for imparting to the yarn the desired amount of twist. The yarn is guided on to reel H by the thread guide J, which is moved to the right and to the left alternately—to the left by means of connection K and a heart cam (not shown), and to the right by means of spring L when the heart cam presents its gradually decreasing radius to the anti-friction bowl at the end of the rod K. The silk remains on the reels H until it is washed with acidulated water, bleached, and dried.

Other Applications of Viscose.—The numerous applications of viscose, independently of its transformation into artificial silk threads, its plasticity, and its comparative cheapness, render it a useful and interesting substance. Several patterns and articles, into the manufacture of which viscose enters, were exhibited in class 87 at the Paris Exhibition of 1900.

(1) Decorative painting with cellulose as base : The collective power of dissolved cellulose (viscose), which is capable of retaining nearly twenty times its weight of mineral powder, is very suitable for forming the base of a paint which, due to the stability of cellulose, resists successfully atmospheric influences. This paint adheres perfectly to plaster even before the latter is quite dry ; to wood, cements, and even to felt and bitumen cards. It is incombustible, and yields a smooth and homogeneous surface that can be washed with soda a few days after the paint has been applied.

(2) Paper for art impressions : The characteristic features of paints with cellulose as base render them particularly suitable for the manufacture of paper for art impressions ; a surface of remarkable smoothness and exceptional softness can thus be obtained, upon which it is possible to engrave figures possessing that finish which is typical of high-class reproductions.

(3) Lining or covering for fabrics : Employed pure or slightly loaded, viscose forms on the surface of fabrics a very homogeneous layer, which is insoluble in water, and which resists effectively the action of acids and alkalis ; transparent viscose can be used on cloth for blinds, and opaque viscose used on cloth for waterproof bed covers and for book-binding. When prepared for the latter purpose it forms a surface which is admirably adapted for engraving and goffering.

(4) Viscose—indiarubber : Viscose mixed with indiarubber is a cheaper substance than pure rubber, and may be used for practically all purposes for which rubber has formerly been used—*e.g.*, waterproof garments, tubes, etc. In combination with viscose, indiarubber resists atmospheric action better than pure rubber, and its flexibility is entirely preserved.

(5) Embossing and finishing effects on fabrics and threads : Viscose can be used very economically as a layer for receiving colour impressions, especially white. On fabrics or threads it forms a cellulose finish that is unaffected by washing. In

dyeing, viscose forms a mordant for certain colouring matters, thus effecting an economic use of dyewares.

(6) Papers, cardboard : Employed in the manufacture of cards and of stout paper for packing purposes, viscose adds additional strength, which varies from 30 to 100 per cent. according to the compositions of the mixture. In a similar way viscose leather papers or mock-leathers have been made.

(7) Compressed viscoid : In virtue of its adherent qualities Viscose yields compact substances of every form. This product is an excellent insulating substance for heat and electricity, and is known by the name " Viscoid."

(8) Various industrial substances : Transparent films of all colours for various purposes have been made from Viscose ; packing papers for soap and similar fatty substances ; transparencies for use as imitation stained glass windows and other purposes ; coloured balloons or globes for electric light illumination ; thick and strong films for replacing celluloid in numerous ways.

Cellulose Esters : Cellulose regenerated from viscose esterifies much more readily with anhydrides and chlorides of acids than does ordinary cellulose. The tetracetate of cellulose in particular is obtained by mixing intimately hydrate of cellulose with a concentrated solution of magnesium acetate, in the proportion of two molecules of the acetate for one molecule of cellulose. To this mixture, which is made homogeneous and dried at 110° C. (230° F.), is added two molecules of acetyl chloride for each molecule of magnesium acetate. The action of acetyl chloride must proceed progressively and with caution, so as to prevent the temperature rising above 30° C. (86° F.). The product is afterwards treated with water to remove the magnesium salts ; it is then dried and exposed to the action of a solvent to separate the cellulose acetate from the small quantity of uncombined cellulose. This solution is clarified and filtered, and then is evaporated, the residue being the ester in a pure state. The product thus obtained— tetracetate of cellulose—resembles very closely nitro-cellulose, but it is distinguished from it by not being explosive ; indeed, it is not even very combustible. It dissolves in chloroform, methyl alcohol, epichlorhydrin, ethyl benzoate, glacial acetic acid, nitro-benzene, etc.

These solutions furnish films of perfect transparency and absolute continuity even when they are so thin as to produce

interference colour effects. They are impermeable to water, and offer great resistance towards the action of reagents. For saponification they must be boiled for several hours with an alcoholic solution of caustic soda ; but even then disintegration does not take place, and the film preserves not only its form, but also its transparency.

Since the publication of the second French edition (1909) of this work, the Viscose industry has made great progress in the method of manufacture (both chemically and technically), and also in the quality of the thread produced. The large dividends that are now being paid by the Viscose silk manufacturers are the best proofs that these works have entered definitely into a period of industrial prosperity. Some real progress has also been made in the cuprammonium process (to mention only " la Soie Bemberg," Adler-silk), and it still appears possible to supply larger quantities by this process than by the Viscose process. The Viscose process is, nevertheless, very much in favour, as is clearly shown by the number of new works that have been erected, and which are still being erected, in various parts of the world ; we may mention amongst others Courtaulds, Ltd., in many parts of England, and Fr. Küttner of Pirna, Germany. Then, again, the Glanzstoff Fabriken of Elberfeld and Mulhouse, which for many years have manufactured so successfully their well-known silk by the cuprammonium process, bought the works and the Viscose processes of the Prince of Donnersmarck a few years ago. This action on the part of the Glanzstoff Fabriken may be explained by the fact that the original patents of this firm will shortly expire, whilst some new and important improvements in the cuprammonium process are in the hands of competitors ; on the other hand, the Glanzstoff Fabriken have introduced many improvements relating to the Viscose process, which, in combination with the Donnersmarck patents and processes, present great advantages. At the Elberfeld works of the Glanzstoff Fabriken, where artificial silk is manufactured by the cuprammonium process, a plant for the manufacture of Viscose threads is already established.

Some years ago the managers of the Glanzstoff Fabriken, in their report to the shareholders on this subject, said : " The artificial silk industry has become relatively precarious, and the large German works which use the Chardonnet process

have for the second time announced a deficit. We have here in Germany to encounter considerable general expense, and we cannot compete successfully with the products that more favoured foreign competitors (especially Belgian) put upon the German market." The Glanzstoff Fabriken then complain of their workmen, of high tariffs for the transport of merchandise (raw materials), of supplementary taxes, etc. They hope, however, with the Viscose process—which requires a smaller quantity of raw material—to be able to place themselves in a more advantageous situation for production, although the works "Donnersmarck" have been run at a loss for some years. This report terminates with the assurance that the manufacture of silk by the cuprammonium process will not be abandoned, but will continue to supply the markets with Barmen and Plauen lace and braid, and to make more and more assured the silk industry of Saxony, where the Viscose process has not been introduced. On the other hand, the artificial silk manufacturers of Belgium, for example, who follow the Chardonnet process, yield as good profits as any firm employing either the cuprammonium or the Viscose process, which again goes to prove that above all it is necessary to carry out the work under favourable conditions, and that it is not yet a question of this or that process supplanting another.

Remarks Concerning the Manufacture of Viscose Silk on an Industrial Scale.—The raw material for the manufacture of Viscose is wood pulp freed from grease and bleached, similar to that which is used in the manufacture of paper. It is used in preference to cotton, because it is cheaper. Although this pulp is often delivered ready for use at the artificial silk factory, it is always a wise plan first to wash it well with a large quantity of water. In general this wood pulp is not sufficiently free from grease ; in this state it cannot be satisfactorily employed for the Viscose process, and should be submitted to a process somewhat similar to the following : In a boiling kier of a similar type to that which is used in the preparation of cotton (see Fig. 7. bet. pp. 34 and 35), the wood pulp is subjected to boiling for about $3\frac{1}{2}$ hours in a bath of soda of $1\frac{1}{2}°$ to $2°$ Bé. Ferruginous or calcareous water must on no account be used in this process. After the pulp has been boiled, the soda lye is allowed to flow out, the substance is well rinsed with water, preferably at a temperature of $25°$ to

30° C. (77° to 86° F.), and finally it is placed in a hydro-extractor. The wood pulp thus treated is transformed into alkali-cellulose in the following manner : After the processes of washing and hydro-extracting, the pulp contains from 40 to 50 per cent. of water, and it is essential that this percentage should be determined accurately. For this purpose a sample of the partially dried pulp is heated to a temperature of 103° to 105° C. (217·4° to 221° F.) until there is no further diminution in weight. The difference in the weights of the partially dried and perfectly dried pulp clearly gives the amount of water, and with tables, such as are used in the conditioning of yarns and fibres, the percentage of moisture can be obtained. According to the researches of Francis Y. G. Beltzer, of Paris, 200 grms. (0·44 lb.) of caustic soda at 26° Bé. are required to transform 100 grms. (0·22 lb.) of cellulose (in this case wood pulp) into 300 grms. (0·66 lb.) of alkali cellulose ; but the percentage of moisture in the partially dried pulp must be taken into account in order to arrive at the exact amount of caustic soda required. The duration of the action of the caustic soda on the pulp must be extended in the manufacture until a uniform alkali-cellulose is obtained, and to achieve this end it is necessary from time to time to make trials to determine when the impregnation is complete. This operation demands much care and attention when the manufacture is carried out on a large scale, and it is necessary to choose mixing tanks in which the work may be quickly performed, and in which all the cellulose will be impregnated uniformly in a relatively short time—about $3\frac{1}{4}$ hours. The mixing tanks that we have described and illustrated for the manufacture of artificial silk by the cuprammonium process are not suitable for the Viscose industry ; it is advisable for this process to use mixing tanks somewhat similar to that illustrated in Fig. 48. The wood pulp is introduced into the cylinder A ; the apparatus is then put into motion and at the same time the soda liquid is allowed to enter by pipe B. The alkali-cellulose obtained by this process is in the form of a bleached pulp, which is removed from the mixing tank at the opening C (where the hinged door is shown in the dotted position), into the wagon D, in which it is carted to the apparatus illustrated in Fig. 49, where it is transformed into Viscose. In the figure the mixing tank A is similar to that in Fig. 48, but jacketed, the interior case being lined with nickel. The

alkali-cellulose previously prepared for transformation into Viscose paste is introduced by the opening B in the dome C. Suppose there are 200 kgs. (440·8 lbs.) of alkali-cellulose to be
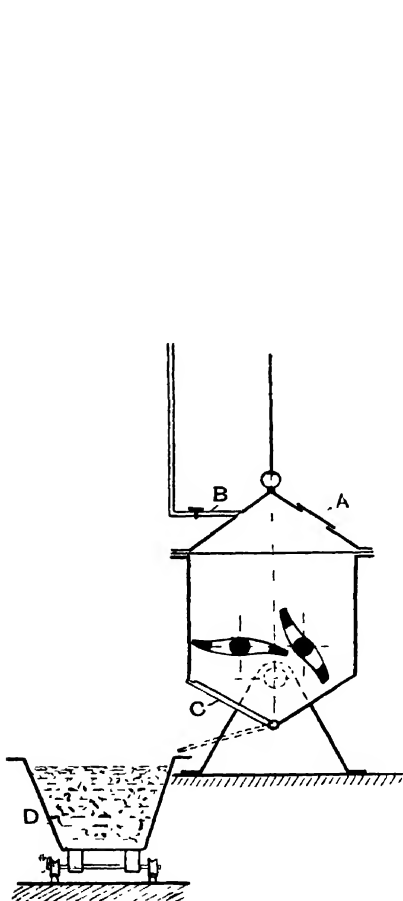
FIG. 48.
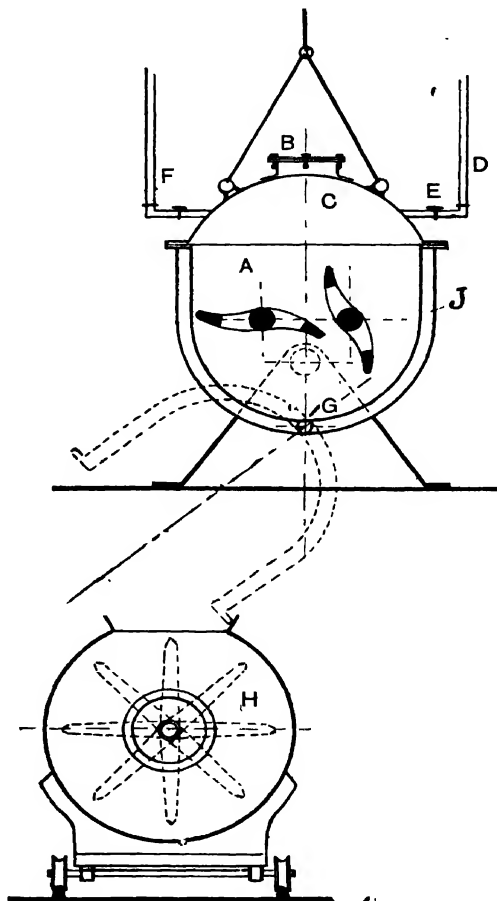
FIG. 49.

transformed into Viscose; after this quantity has been placed in the mixing tank A, the lid B is hermetically sealed; the agitators are then set in motion, and are kept rotating for twenty to thirty minutes. Carbon disulphide flows through the pipe D, and the necessary quantity is admitted into tank

A by opening the valve E. For the transformation of the 200 kgs. (440·8 lbs.) of alkali-cellulose, 34 kgs. (74·936 lbs.) of carbon disulphide are required. The ingredients must then be mixed for three or four hours in order to obtain a homogeneous substance which has a dark yellowish-orange colour. After the process of mixing has been in operation for the time indicated, 200 kgs. (440·8 lbs.) of caustic soda, made up into a 15 per cent. solution, are added to the mixture, and the mixing is continued until a uniform pulp is obtained ; the caustic soda comes from a graduated reservoir through pipe F. The Viscose thus obtained is then deposited into the mixing tank H, mounted on a wagon, by rotating mixer A bodily about the axis G until it reaches the dotted position. The Viscose is then diluted with water in mixing tank H, in the proportion of 185 litres (40·7 gals.) of water to 100 kgs. (220·4 lbs.) of Viscose pulp. It is desirable during all these operations that the temperature should not exceed 25° C. (77° F.), and when these operations are completed that the mixing tank A should be cooled by allowing a freezing mixture to flow through the jacketed part J. The solution is then mixed for 4 hours in the apparatus H, and finally allowed to stand for 10 to 14 hours ; during this time liquefaction proceeds gradually, and it must be arrested when the consistency of the substance is most favourable for transformation into threads ; this point is determined by means of an instrument termed a viscometer. If this point is passed, liquefaction continues, followed some time after by decomposition, with later a solid deposit of cellulose. Before the solution is spun— an operation which is performed under a pressure of three to four atmospheres—it is filtered and the air bubbles are removed from it by an aspirator. The machines for the spinning of Viscose are very similar to those used in the cuprammonium process—slight differences being found, in different factories, in what are considered similar types of machines. In a later part of this work we shall have occasion to indicate supplementary parts of these machines, and also improvements made by different inventors.

CHAPTER XIV

Lustre Artificial Silk

LUSTRE ARTIFICIAL SILK PRODUCED BY A SOLUTION OF CELLULOSE IN ZINC CHLORIDE.—This solution is used in the manufacture of filaments for electric lamps. The threads are comparatively weak, but are quite strong enough for this purpose. This weakness is in a great measure due to the method of preparing the solution. Ordinary cellulose is only slightly soluble in cold zinc chloride, in which it becomes a gelatinous substance ; a real solution is obtained only with a high temperature. Without doubt the zinc chloride, by its hydrating action, produces depolymerization of the cellulose, such that the substance precipitated possesses only in a slight degree the characteristic properties of cellulose. Wynne and Powell (who, in 1884, introduced the process of forming artificial silk filaments—or, rather, filaments for electric light globes—from a solution of cellulose in zinc chloride by the squirting method) tried to replace the zinc chloride by a mixture of zinc chloride and aluminium chloride. It is possible that depolymerization may be retarded somewhat in this manner ; but Wynne and Powell, as well as Dreaper and Tompkins— who have also proposed to employ cellulose dissolved in zinc chloride to produce a textile thread—have been able to obtain this solution only by raising the zinc chloride to a high temperature. However, it has been stated that during these processes the molecular constitution of the cellulose is changed, and the threads thus formed are exceedingly weak. In an American patent, Bronnert describes a method which, so far as we know, has not yet passed beyond the experimental stage ; according to this method, it would be possible to obtain a strong thread by subjecting the cellulose to preliminary processes before dissolving it in zinc chloride, just as was done for the cellulose dissolved in an ammoniacal solution of copper oxide.

The most advantageous method consists in transforming the scoured and bleached cellulose into sodic cellulose by immersing it in a cold bath of concentrated caustic soda, then decomposing the sodic cellulose with water, and finally in

dissolving the cellulose thus obtained in a concentrated solution of zinc chloride. The solutions prepared in this manner must be kept in tanks and at a low temperature, so as to prevent any decomposition which would be detrimental to good spinning, and might even make this operation impossible.

A new process, and one which appears to have a future, is that of the alkali cellulose by J. G. Beltzer, of Paris. When wood pulp is introduced uniformly into a caustic soda lye of 10° Bé. (density 1·0744) and at a temperature of 0° to 5° C. (32° to 41° F.), hydration takes place ; an almost complete solution is obtained only when the temperature is lowered to − 10° C. (14° F.). With these solutions of alkali cellulose the inventor has been able to produce artificial silk, pellicles, etc. Again, Beltzer[1] observes that, like solutions of caustic soda, sulphuric acid, phosphoric acid, etc., when employed at the proper concentration, mercerize or hydrate cellulose. Sulphuric acid, for example, at 49° to 55° Bé., transforms cellulose into a parchment-like substance which dissolves in the cold and forms a viscous, homogeneous, and transparent mass. This solution is termed amyloid because of its resemblance to amidon (starch). The same result is obtained by treating cotton cellulose or wood pulp with zinc chloride, or with phosphoric acid at a certain concentration. The action of these agents on cellulose has been known for a considerable time ; but it has been left for J. G. Beltzer to make experiments at low temperatures of 0° C. to − 10° C. (32° to 14° F.), by which he has been able to prevent hydrolysis and destruction of the cellulose. As soon as a gelatinous solution of hydrated cellulose is obtained at this low temperature, the solution is diluted with cold water, preferably with ice, to avoid too great a rise in temperature. It then forms a precipitate of hydrated cellulose, which is washed in water, or in a bath that is slightly alkaline, to remove the acid ; after a final washing with cold water a pure hydrated cellulose is obtained which dissolves completely in caustic soda lye.

[1] *Les Matières Cellulosiques.*

CHAPTER XV

Acetate Silk or " Celanese "

THE latest type of artificial silk to become permanently established is that known as cellulose acetate silk. It is only natural to find that many different methods have been tried in the evolution of this product. In some cases, the viscous liquid was made from cotton or wood pulp and acetic anhydride in the presence of a suitable catalyst. The resulting compound was then dissolved in acetone, the acetate dissolved in a mixture of organic compounds to obtain the correct degree of viscosity, and the final mixture spun by one or other of the prevailing methods of preparing artificial silk yarns.

By far the greatest number of experiments in regard to the manufacture of cellulose acetate silk have been made by The British Celanese Limited, London and Spondon, Derby. This firm is the sole manufacturer of the products known as " Celanese," and the word " Celanese " is their registered trade name for cellulose acetate silk manufactured by them. Hosiery yarns, warp and weft yarns for weaving, woven fabrics, and other textile products are now extensively manufactured from " Celanese." Very similar products, under the name of acetate silk, are now made by a few firms.

The basic substance was used during the war as a dope for aeroplane fabrics, and for this purpose was made hard ; but when yarns were made for textile purposes, it was, of course, necessary to make them quite supple ; this was done successfully, and it is claimed that " Celanese " products, in general, are softer than other artificial silks, have a higher elasticity factor, a finer filament, and a higher breaking strain—particularly when wet. Many of the original acetate silks were deficient in this respect, but the defect has evidently been overcome in " Celanese " yarns.

The difficulty of dyeing acetate yarns formed, perhaps, the chief objection to their use for textile purposes. Within recent years, however, this and other drawbacks have been removed —so much so that this new form of artificial silk has made great advances, and has become a practicable and successful commodity for the textile industry. It is quite probable that greater developments will obtain in the near future. This

satisfactory state of affairs has been obtained partly by a new range of dyestuffs, known as the S.R.A. Dyestuffs for "Celanese," and which has been developed by The British Celanese Limited. These colours are particularly suitable for dyeing their patented products, are used by the Company for dyeing their own goods, and are sold to dyers for the dyeing of textiles made wholly or partially from "Celanese" yarns.

For a considerable time the operations of dyeing "Celanese" were fraught with great disadvantages; indeed, so much difficulty was experienced in obtaining satisfactory results that the Company deemed it advisable, if not necessary, to establish their own dyehouse and to make their own dyestuffs. The use of their S.R.A. dyestuffs, and the methods of dyeing, have enabled the dyeing process to be conducted with ease.

"Celanese" yarns, fabrics and knitted goods have a great affinity for these S.R.A. dyestuffs, whereas other goods made from different fibrous materials, or by different artificial silk processes, have not the same affinity for these dyestuffs. Further "Celanese" products do not take on the same degree of red as cotton does when both are dyed by cotton dyestuffs; hence, the two fibrous materials may be mixed in various ways, and, when dyed in the same bath, two different tones or tints are apparent in the same yarn or fabric. For example, a "Celanese" yarn may be twisted with another kind of artificial yarn, and the compound yarn, when dyed, will possess two distinct shades or colours. A common method is to use "Celanese" as warp, or as weft, in conjunction with another type of artificial silk in Jacquard weaving, so that the ground of the fabric is developed by one kind of yarn and the decorative portion or figure developed by the other yarn. Cotton and artificial silk are similarly combined. Then, when dyed, the two parts—ground and figure—differ in colour. This effect is sometimes obtained by two dyeing operations, and at other times by one operation. Solid effects, or marled effects, are thus easily obtained, according to the structure and kind of the yarns used.

It has already been stated that the viscous liquid used for cellulose acetate silks, including the patented "Celanese" methods, is made from cotton or wood pulp, and when the desired degree of viscosity obtains, the solution is ready for the operation of spinning or drawing, the exact details of which form more or less secret operations; it will be understood,

however, that some of these operations, especially that of determining the thickness of the yarn, may resemble in principle those already described in connection with the spinning of the older types of artificial silk.

The softness of " Celanese " silk is probably due to the high number of filaments that constitute the yarns, and its strength and regularity are probably due to the same structural causes. The so-called " filament denier " in "Celanese" is very low, e.g. 0·5, 1·0, 1·5, 2·0, 5·0. Many other types of artificial silk have a much higher " filament denier," in some cases as high as 12 or even more. This " filament denier " divided into the denier count gives the number of individual filaments in the yarn. For example, in a 150 denier silk, with a " filament denier " equal to 5, there would be—

$$\frac{150}{5} = 30 \text{ individual filaments.}$$

A most essential property in any textile yarn is strength, not only in the dry state, but also in the wet state, for both yarns and the fabrics made from them are subjected to considerable contact with water and other liquids both during the processes of manufacture and while in domestic or commercial use. From a series of sea water tests it has been proved that " Celanese " threads before immersion had an individual breaking load of 3·2 kilos (7·05 lbs.), whereas after the threads had been immersed for five weeks, the breaking load was 3·0 kilos (6·6 lbs.)—almost a negligible difference.

Again, from bio-chemical tests conducted in the South of England, it was found that whereas silk, cotton and linen rotted in four to seven weeks, " Celanese " was scarcely affected. It would thus seem that " Celanese " is a suitable substance for use in the manufacture of lines, nets and the like.

Finally, " Celanese " is an excellent insulator, and is now largely used in the electrical industry. As a matter of fact it is often used for Post Office telephone and for insulation purposes generally.

CHAPTER XVI

The Recovery of By-products in the Cuprammonium Process

WE have seen that artificial silk results from the coagulation of° solutions of cellulose accompanied or followed by the elimination of the solvents. These solvents, which are expensive, must be recovered in order that the artificial silk may be produced at a remunerative price.

(1) The first by-product recovered is the ammonia gas which is carried away by the air used for oxidation in the formation of ammoniacal copper oxide. This ammonia vapour is simply collected in water, or else in concentrated sulphuric acid, with the formation of ammonium sulphate.

(2) The recovery of the copper and of the ammonia contained in the precipitating liquids. The methods of recovery of these by-products differ according as sulphuric acid, soda, or potash is used.

Let us consider first the method of recovery of copper and of ammonia from a sulphuric acid solution. At the commencement of Chapter XII, page 87, we mention the method employed for recovering the copper from the silk made by the piecers at the spinning frame. The acidulated water charged with copper and ammonium sulphate, as well as the very weak sulphuric acid which has been used for precipitation in the spinning frame, and which is also charged with copper and ammonia, is forced forward by a lead injector into a large wooden cistern of about 25 cu. metres (32·75 cu. yds.) capacity. In these cisterns the copper is recovered by immersing bars of iron, as free as possible from rust, into the acid. The copper which is deposited is removed periodically, dried, and sold ; or it can be employed again in the manufacture of the ammoniacal copper oxide.

When the copper has been thus recovered, preparations are made for recovering the ammonia ; this may be accomplished in two ways : (a) The simpler method is to evaporate the liquid, say, in a Kestner evaporating apparatus, or else in a lead-lined cistern provided with a steam coil. The ammonium sulphate is deposited as the evaporation proceeds, and, after having been dried, is then sold. It is a good plan to filter the

liquid before evaporation in order to arrest particles of iron oxide, of copper, and of other impurities which would stain the salt. It is important that the yield of ammonium sulphate should approach as nearly as possible that amount which, theoretically, would be obtained from the quantity of ammonia employed. One litre (0·22 gal.) of ammonia at 20° Bé. should produce 870 grms. (1·91 lbs.) of ammonium sulphate.

The total should be obtained by adding together the products of the two processes of recovery, and observations should be made at the beginning of each month of—

(*a*) The quantity of ammonium sulphate recovered from the copper columns.
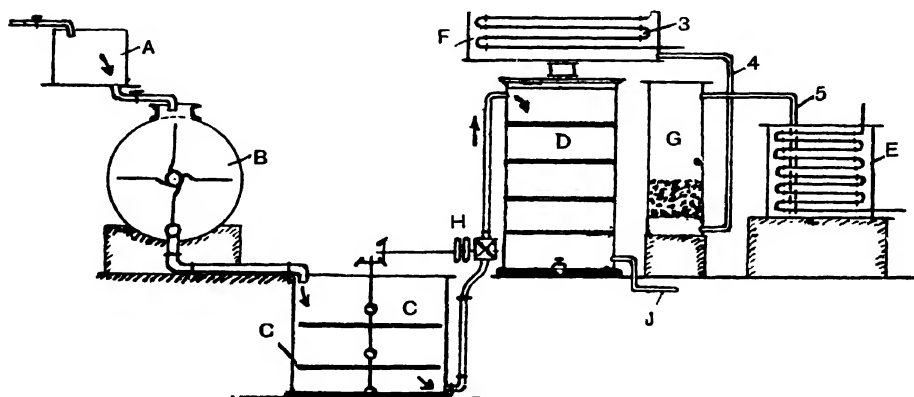
Fig. 50.

(*b*) The quantity of ammonium sulphate from the large wooden cisterns.

(*c*) The quantity of ammonium sulphate obtained from the evaporating apparatus.

(*d*) The quantity of ammonia from the columns, mixing tanks and pipes.

The amount contained in the pipes from the cisterns to the spinning room being a constant quantity, it is really only necessary to ascertain the amounts in the other parts ; this is done by means of a graduated scale fixed along the levels of the liquids.

Another, but more complicated, method is as follows : About 2000 litres (440 gals.) of the acid, which has been used for precipitation, and from which the copper has been extracted, is allowed to flow into a graduated tank A, Fig. 50, and then

into a mixing tank B.   To this acid is added 60 kgs. (132·24 lbs.) of ammonium sulphate, and 685 litres (150·7 gals.) of calcined chalk.   Ammonium sulphate is added to the mixture for the purpose of replacing the ammonia that is lost during the manufacture—by filtration, in the spinning frame, and by leakage of the apparatus—for, in addition to the recovery of the ammonia, it is proposed to produce with this installation all the ammonia that is necessary for the work.   The mixture flows from the first mixing tank B into a large mixing tank C, and is forced from here through a connecting pipe by the rotary pump H into the distillation vessel D.   A jet of steam enters at J, and travels from bottom to top through the mixture as the latter flows slowly from top to bottom over the overlapping plates 1 and 2 of the column D, Fig. 51.   The ammonia gas is thus carried with the steam, and reaches the condenser F, Fig. 50, which is provided with a condensing coil 3.   The water is in consequence condensed, and flows back, while the gas passes through pipe 4 and is purified in its passage through the coke in column G ; it finally emerges by means of pipe 5, and is condensed in the last coiled condenser E.   It is then ready to be used again in the formation of ammoniacal copper oxide.
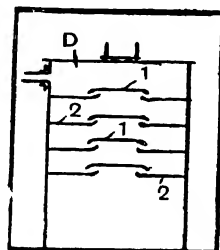
Fig. 51.

(3) When the coagulation at the spinning frame is effected by means of soda or potash, the copper is removed advantageously by electrolysis, and the ammonia is obtained by evaporation.   R. Linkmeyer, in his patent No. 353187 (French), proposed to recover part of the copper by the introduction of flakes of cotton cellulose into the precipitation bath ; the cellulose retains the copper, and could be used for solution in ammoniacal copper oxide.

(4) E. Crumiére, of Paris, has suggested a method of removing the copper from the threads, and at the same time of recovering the copper by means of an electric current, as had already been proposed in 1890 by Henri Despeissis.   In the Crumiére factory, however, the process is carried out as follows*: The removal of the copper from the artificial silk threads or from artificial hair, is effected as usual by the action of dilute acid ; we should mention in passing, however, that the process is relatively long and costly.   As the threads in

formation lack solidity, they are wound on to bobbins before being freed from copper ; but, as already stated, the action of the acid for the removal of copper is slow, especially on the inner layers of threads on the bobbins ; in addition, large quantities of acid are required which are rapidly used up, and which must be often renewed. By the Crumiére invention it is possible to remove the copper almost instantaneously, and with much smaller quantities of acid. In addition to the quick recovery of the copper, the liquid can be used a large number of times. The new process consists in placing the
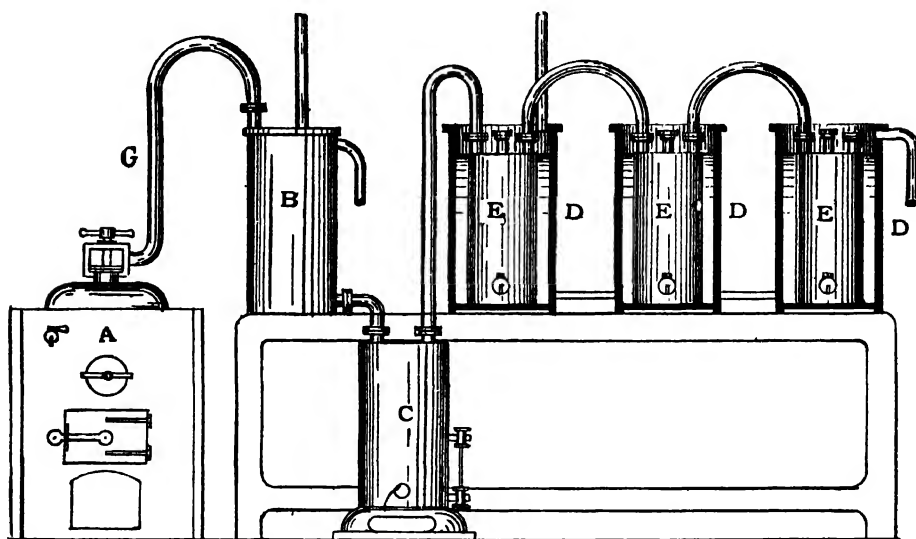
Fig. 52.

bobbins of silk, containing after precipitation ammonia and copper, into a bath filled with acid—for example, sulphuric acid diluted with water—and in passing an electric current through this liquid. The threads lose their colour immediately, the copper being dissolved by the acid, and carried to the cathodes, where it is deposited, whilst the acid employed is regenerated continuously. The silk which has thus been freed from copper is then washed in water and dried under tension. The Crumiére processes are conducted in the works of a French company at Flaviac (Ardéche) and at Mysskow in Poland.

La Société Anonyme " Le Crinoid " of Rouen reduces the copper salts in the alkaline baths by adding $1\frac{1}{2}$ per cent. of a solution of formaldehyde to the precipitating liquid, which itself is kept at a temperature of 40° C. (104° F.).

The apparatus illustrated in Fig. 52 is used for extracting ammonia from the ammoniacal liquor that comes from gas-works or from ammonia factories. This apparatus consists of boiler A, condenser B, tank C, cooling basins D, with absorption surfaces E. About one-third of the boiler A is filled with the ammonia water from the gasworks, and with powdered calcined lime. Then each vessel E is filled with water up to two-thirds of its height, and the boiler A is heated either by fire or by steam. The ammonia gas escapes from the liquid along with water vapour, passes through the pipe G into the coil of condenser B, then into the tank C, which retains the tar, and finally into the cylinders D, where the gas is dissolved in water. If ammonium sulphate is used, it is dissolved in water, and this solution is treated in the same manner as the ammonia water from the gasworks.

CHAPTER XVII

Solutions of Cellulose, and the Preparation of Solvents

PREPARATION OF CELLULOSE BY THE GLANZSTOFF FABRIKEN PROCESS.—When ordinary cotton is brought into contact with Schweitzer's reagent, it swells and dissolves only so far as the solvent acts chemically on the cotton fibre. If this operation is carried out at the ordinary temperature, the cellulose is peroxidized, and the solution can no longer be used for the manufacture of artificial silk. If, on the contrary, the solution is effected at a low temperature, and if the copper and the cellulose are used in certain proportions, the threads obtained possess the necessary physical properties. But this solution takes place only slowly ; in order, therefore, to avoid this loss of time, the cellulose is prepared by preliminary processes, and in such a way that a relatively short time only is necessary for the operation. By a prolonged oxidation of the cellulose with a clear solution of chloride of lime, a product is obtained which dissolves easily up to 8 per cent. in a solution of ammoniacal copper oxide. The thread made from this solution is easily dyed with basic colouring matters, and behaves in this case as an oxycellulose. In order to be more sure of obtaining a good result, the solutions are made from cellulose that has been previously hydrated. This is done simply by treating the cellulose with cold concentrated caustic soda, and afterwards washing the sodic cellulose in pure water. Cellulose thus prepared dissolves almost immediately in ammoniacal copper oxide solution kept at a low temperature. It is customary to add to these solutions a little antimony and tannin ; these astringent substances are by no means injurious to the lustre of the thread. The process of solution can be simplified further by treating, at a low temperature, hydrated cellulose with a concentrated solution of caustic soda ; the sodic cellulose thus obtained is then treated in the cold with a calculated quantity of a salt of copper, and the mixture is dissolved directly in ammonia.

Whilst the hydrated cellulose is nearly insoluble in ammoniacal copper oxide solution, it dissolves with

extraordinary ease in the same liquid if it has been previously hydrated by treating it first with a concentrated solution of caustic soda, and afterwards with water.

Fremery and Urban's Process.—The directors of the Glanzstoff Fabriken, Fremery and Urban, give, in their Belgian patent, a lengthy description of a preparatory treatment of cellulose with a view to its direct solution in ammoniacal copper oxide. The patent states : " By our invention we are able considerably to augment the action of solvents on cellulose by an energetic preparatory treatment with ordinary bleaching agents, oxidizing or reducing, or with agents such as sulphites, sulphurous acid, sulphuric acid, a solution of soda, a solution of soda and carbon disulphide ; the cellulose can then be converted into hydrocellulose, as happens during the treatment with weak mineral acids, or by the parchmentizing process. We obtain a solution of cellulose in the known solvents not only in a much shorter time, but in more than double the quantity. The following example will show the process quite clearly : If commercial cotton, cleaned and unbleached, or bleached slightly—cleaned cotton wadding, for example--be treated with a solution of ammoniacal copper oxide, not more than 3 to 4 per cent. of this cellulose goes into solution ; in addition, several days are required for the process. If the same kind of cotton, however, be made to undergo an energetic preparatory bleaching—that is to say, if it be left, for example, from 12 to 18 hours in a bleaching liquor which contains 15 grms. of chloride of lime per litre ($2\frac{1}{3}$ oz. per gal.) —it will, after being washed and dried, dissolve in the same solution of ammoniacal copper oxide in the proportion of 10 per cent., or even more, and this in the space of a few hours. With a more energetic process of bleaching it is possible to obtain, for example, solution in ammoniacal copper oxide, no longer a viscous and sticky substance, but a liquid product that is unsuitable for the subsequent industrial treatment to which solutions of cellulose are usually submitted in the manufacture of artificial silk. The action of the bleaching liquor depends upon the concentration of the oxidizing or reducing agents present, as well as on the duration of the action. The action varies for different kinds of cellulose ; indeed, a relatively weak bleaching liquor produces the desired effect on cotton, whereas a more energetic treatment is required for ramie fibres. Cellulose that has been parchmentized by

treatment with concentrated sulphuric acid, and which is designated generally by the name of amylöide, dissolves in ammoniacal copper oxide solution in a much higher proportion than does cellulose which has not been prepared under these conditions. Thus, for example, parchment paper produced by means of sulphuric acid, or by zinc chloride, dissolves in a proportion of 10 per cent. and over. A solution of amylöide of this nature can be used for the manufacture of artificial silk of the same count as is made from a solution of cellulose. It will thus be seen that hydrocellulose dissolves in a proportion as high as that of cellulose prepared by an energetic bleaching process. Hydrocellulose can be obtained by treating pure cleaned cellulose, say, cotton wadding, with sulphuric acid at 3 per cent., pressing it without washing, and leaving it in contact with the air to dry. After the substance has been dried completely at a temperature of 40° C. (104° F.) it is washed and dried again.

"We mention here only one of the different methods of transforming cellulose into hydrocellulose. The application of parchmentized cellulose is more or less advantageous according to the degree to which the process of parchmentizing has been carried—that is to say, according as the cellulose has been more or less transformed into an amorphous and transparent substance. Sulphitic cellulose and sodic cellulose obtained respectively by the action of a sulphite solution and of a soda solution dissolve likewise in a much higher proportion than ordinary cellulose. The preparatory treatment aimed at in the present invention appears to produce to a certain extent a sort of unfolding or opening out of the cellulose, determined generally by the destruction of the cuticle which envelops the natural cellulose in such a way that the cellulose enters then into direct contact with the solvent employed. This preparatory treatment should be carried out in such a way that the foreign matter, which accompanies the cellulose, is completely destroyed; otherwise a fundamental decomposition of the cellulose molecule would result. Our experience has also demonstrated to us that chemically pure cellulose, such as is separated, for example, from an ammoniacal copper oxide solution, dissolves in a proportion as high as' that of cellulose prepared under the conditions described."

The Foltzer Process (French Patent No. 345,687).—This is an industrial process for the manufacture of a hydrated

cellulose up to 10 per cent., dissolving in the cold in a direct solvent in less than 24 hours. With these cellulose solutions one obtains—in the cold and under a pressure not exceeding two atmospheres—a product of artificial silk which fulfils all the conditions demanded for textile purposes ; a fine, pliable, and lustrous artificial silk, equal in strength to natural silk, and not loaded with water. To obtain this product the fibres of ordinary cotton, or of other vegetable subtances with cellulose as a base, are crushed and reduced to pulp, and then treated with a solution of sodium carbonate and caustic soda in approximately the following proportions : 100 kgs. (220·4 lbs.) of cotton for 1000 litres (220 gals.) of solution, to which are added 30 kgs. (66·12 lbs.) of sodium carbonate and 50 kgs. (110·2 lbs.) of caustic soda. The mixture of cotton, alkali and water is hermetically sealed in a tank or kier. The cotton fibres are disposed in layers between grills or perforated iron plates ; while the solution, at a temperature of 119° C. (246·2° F.), and under half atmospheric pressure, is withdrawn and returned by a rotary pump, a continuous circulation of the liquid being thus obtained. The solution is made to pass through the layers of cotton during the whole time of boiling, which lasts about four hours. It is an advantage to use a heating coil in this kier, so that during the circulation the solution may be kept at an approximately constant temperature. However, the present invention does not deal with the arrangement of the apparatus, but with the process itself, the percentage of the chemical agents which are used, the time of the operation, and the temperatures and pressures which obtain during the boiling.

The proportion of 100 kgs. (220·4 lb.) of cotton to 1000 litres (220 gals.) of solution is not absolutely constant ; on the contrary, it varies according as the constitution of the fibre is more or less pure cellulose. When wood or any other vegetable substance with cellulose base is used for this manufacturing process, it is necessary to ascertain the percentage of cellulose which enters into its constitution ; by doing this we get the necessary number of kilogrammes or pounds which has to be treated in the above 1000 litres (220 gals.). To find this proportion it is customary to take as a standard, 100 kgs. (220·4 lbs.) of cotton as near pure cellulose as possible for the 1000 litres (220 gals.) of the above-mentioned solution

A beneficial effect results if the concentration of the cellulose

in water is at least 12 to 15 per cent. when it is placed in contact with the solvent, for under these circumstances the solvent acts more rapidly. The humidity of the surrounding atmosphere has naturally a certain influence on the duration of the solution.

In another part of this work we have stated that cotton fibres—especially those that have been slightly bleached—when introduced into a solution of ammoniacal copper oxide, first shrink, then swell and partially decompose, and finally dissolve altogether. The action of the cuprammonium liquor on cellulose was first observed by John Mercer, and then by Schweitzer, both of whom have described the conditions which are most favourable for the treatment. Many later scientists, and among them A. Herzog, of Sorau, Wiesner, and Hassansek, have thoroughly studied the behaviour of cellulose, and in their works have published their interesting observations, and introduced micrographic illustrations showing the alterations in structure which take place in the cellulose. If, with a microscope capable of enlarging from 200 to 300 diameters, we examine a cotton fibre that has just been placed in contact with cuprammonium liquor at a low temperature, we shall see an immediate swelling of the fibre, which is soon followed by decomposition and complete solution. Take, for example, a fibre of bleached cotton from a sample of long-fibred material with an average length of 40 to 45 millimetres ($1\frac{1}{2}$ in. to $1\frac{3}{4}$ in.), and place this fibre between two thin cover glasses in the presence of a drop of cuprammonium liquor, and in such a manner that the liquid may come in contact with one of the ends of the fibre. The phases through which the fibre passes can then be seen up to the point of complete solution. Consider, for example, Fig. 53, which represents a cotton fibre under treatment, and with which a drop of ammoniacal copper oxide comes first in contact with the end A. The solution, which is slowly absorbed by the fibre, passes then to the upper end of part A. At a given moment the fibre will appear somewhat as represented in the figure. At the upper part of A, where the solution ultimately arrives, the fibre is apparently similar in structure to an untreated portion, and the only physical changes in the fibre are a certain amount of shrinkage, gaps in the walls, and a slight spiral twist ; the latter probably accounts for part at least of the shrinkage. At point B the fibre has been under the influence of the liquor for a longer

time, and the degree of shrinkage is greater, the walls of the fibre contain wider gaps, and the swelling gives to the part a globular form. At C, where the treatment has been still longer in operation, the fibre is rapidly approaching the stage of decomposition. At D the original structure no longer exists, and the cellulose is already becoming gelatinized. At E, where the liquid has been in contact with the fibre for the longest period, the action is complete, and the cellulose is dissolved. After the cellulose has been completely dissolved, the homogeneous syrup can at most contain an insignificant quantity of organic compounds. This practice has found an industrial application in the Despeissis process.

The Solution of Cellulose and the Preparation of the Solvents.— We introduce here the Despeissis patent, which forms the fundamental base of the process, and we also recapitulate in some measure the methods employed in the manufacture of artificial silk by the copper process. It is around the patents of Despeissis and Pauly (those by the former are public property, and those by the latter are in the hands of the Glanzstoff Fabriken Company) that the manufacture is concerned. The questions of different temperatures and different concentrations have been discussed. Finally, the last of these patents, dated 1st December, 1897, has long since expired, and the process is therefore public property. This industry has extended considerably within the last two decades. It is remarkable that the inventor, Despeissis, in his laboratory experiments, should arrive at, and mention in his patent, an idea as accurate and as complete as an industrial process, and to see, although rather imperfectly, even the means of manufacturing similar new products.
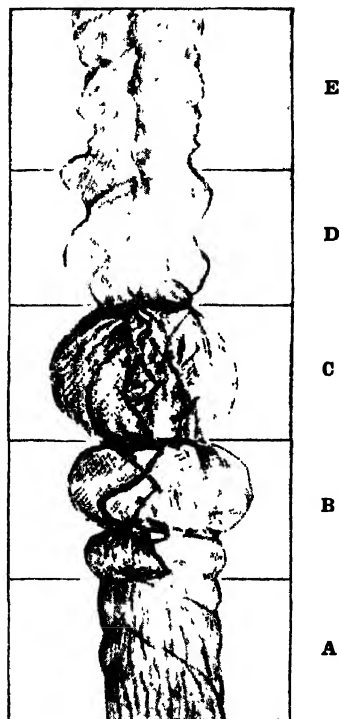
Fig. 53.

The Despeissis Process (French Patent 203,741 of 12th February, 1890, by Louis Henri Despeissis ; after J. Persoz, *Rev. Gen. Mat. Col.*, No. 27, pp. 86–89) : New method of manufacturing artificial silk. The new method of manufacturing silk described in the present patent differs essentially from all those that have been suggested up to the present, not only in the nature of the substances employed, but also in the chemical reactions on which it is based, and by the results which it is possible to obtain. Up to the present time many different methods have been proposed for the manufacture of an artificial product having the appearance of silk, and capable of being spun and woven. All these methods are based on the employment of nitro-cellulose (pyroxyl or gun-cotton) dissolved in a mixture of ether or of alcohol so as to form a collodion either in glacial acetic acid or in some other substance possessing the necessary solvent properties. It is hardly necessary to mention the many serious drawbacks that accompany the use of these processes—processes in which it is necessary to introduce into the operation a body possessing such eminently dangerous properties as pyroxyl.

The filaments of artificial silk that are obtained by the aid of such substances are naturally very inflammable, and their use demands a series of chemical operations which have for their aim the removal, as far as possible, of this tendency to inflammability ; but this result can be attained only partially, and part of the nitric acid employed in the manufacture of pyroxyl always remains combined or mixed with the substance produced. Hence the necessity for adding to it other substances such as salts (phosphates, silicates, aluminium salts, etc.), or of substances such as gelatine. These substances in their turn react in an injurious manner on the quality of the manufactured products, without speaking of the complications which accompany their use in the manufacturing process. In the new process of manufacture, which constitutes the object of the present patent, the use of pyroxyl is completely avoided. The raw material to be used is pure cellulose (cotton, straw, wood fibre, etc.). This cellulose is dissolved in the cuprammonium liquor (Schweitzer's reagent), and the solution thus obtained is stored in a tank from which it is forced out under air pressure through capillary tubes ; the opening of each of these capillary tubes is constructed so

as to give to the issuing jet of viscous liquid the desired diameter after the necessary degree of tenuity has been imparted to the filament formed by coagulation.

On emerging from these capillary tubes, the jet of viscous cellulose liquid, dissolved in Schweitzer's reagent, passes through a special chemical bath, such as dilute hydrochloric acid, dilute sulphuric acid, acetic acid, oxalic acid, weak tartaric or citric acid, alcohol, dilute carbolic or tannic acid, etc., the action of any of which liquids is to coagulate instantaneously the cellulose in solution, and to convert it into a solid filament or fibre, and at the same time to remove the small quantities of copper and of ammonia that have been carried forward by the cellulose. Thence, by means of pulleys, bobbins, drums, or any other mechanical arrangement, the filaments pass into a bath of hydrochloric acid, and remain there long enough to complete the removal, by chemical action, of the remaining copper and ammonia. The hydrochloric acid transforms the Schweitzer's liquor into chloride of copper and ammonium hydrochlorate—substances that are readily soluble, and which separate easily from the filaments ; the latter then remain composed of pure cellulose. The dilute hydrochloric acid bath can be replaced by any other chemical bath provided that it results in the formation of soluble compounds of copper and ammonia, which may be easily separated from the filament. One could also make use of a simple bath of warm water, or, to accelerate the action, make the filaments pass over little pulleys or little platinum or carbon supports joined to the positive pole of a galvanic battery, or to any other electrical source. The negative pole would be in electrical contact with the plates of copper or other metal, which would be partially immersed in the bath. By this action of electrolysis the copper and the ammonia are carried towards the plates, on one of which the copper is deposited as pure metal ; the copper may then be removed from the plate and used again. When the electrolytic action is not employed, the recovery of the copper, which is taken up in the course of the process, may be accomplished by precipitation in the baths, where it would be found in solution.

When the filament of artificial silk thus obtained has been purified by methodical washings, it passes slowly through a hot stove or a tube through which blows a current of hot air ; in either case the moisture is removed until the correct degree

of dryness is obtained. It then only remains to be wound on to drums or bobbins, on which it remains until it is required to be reeled into hanks ready for dyeing, winding, or other processes preparatory to weaving. With the object of making the artificial silk approach still more the composition of natural silk, which contains a certain proportion of nitrogenous matter, one may add to the solution a certain quantity of organic matter of animal origin, such as albumen, waste or coarse parts of silk cocoons, etc. These substances are also soluble in the reagents, and they mix in the process so as to form an integral part of the filament. The filament, as it leaves the last washing bath, may also be made to pass into a solution of albumen greatly diluted with water. To accelerate the solution of the cellulose in Schweitzer's reagent it is a good plan as a necessary preliminary to get rid of the greasy and resinous substances which accompany it ; to effect a high state of division, and to stir the mixture often. When the solution is prepared, it is filtered through sand or through amiantus, a fine variety of asbestos, so as to retain all undissolved particles ; it is then ready to be put into work.

The process of manufacturing artificial silk described in the present patent may also be extended to include the treatment of threads and of fabrics of cotton, flax, ramie, hemp and any other textile material composed of cellulose, so as to give to them the appearance of silk. With this end in view, the threads, before being used in weaving, or those which have already been made into fabrics, are drawn through a bath of Schweitzer's reagent, and the speed of the threads or cloth is regulated in such a manner that their surfaces may be attacked to the proper degree. The threads and fabrics pass immediately from this bath into the coagulation bath already described, then into the refining and washing baths, and are finally removed to be dried. At this stage they have the appearance of silk. Paper may likewise be treated somewhat similarly.

Summary.—The present description claims, in view of its being made the subject-matter of a patent, the principal points enumerated below—

(1) The employment of pure cellulose dissolved in Schweitzer's reagent for the manufacture of a textile filament.

(2) For the manufacture of a textile filament, the employment of pure cellulose dissolved in Schweitzer's reagent, and

coagulated, in the form of a fibre, by dilute hydrochloric acid or any other substance having the same action.

(3) For the manufacture of a textile filament, the employment of pure cellulose dissolved in Schweitzer's reagent, coagulated in the form of a filament by dilute hydrochloric acid, or any other substance having the same action, and then with the object of removing the copper and ammonia which it still holds, immersing it in chemical baths, in water, or subjecting it to electrolysis.

(4) For the manufacture of a textile filament, the production of a fibre after the processes which have just been enumerated, and to which fibre has been incorporated a certain quantity of animal matter, such as the waste or coarse part of silk cocoons, albumen, etc., in view of approaching the chemical composition of natural silk, and of imparting more or less lustre.

(5) For the treatment of threads of cotton, flax, hemp, ramie, etc., before weaving, or of cloths already woven with these threads, the passage through a solution of Schweitzer's reagent, the coagulation, and the washing in a series of baths analogous to those already described.

The whole is the same as has been specified in the course of the present description.

The Process of Dr. Pauly (French Patent No. 272,718, December, 1897).—This process consists of dissolving the cellulose in ammoniacal solution of copper oxide. The cellulose is cleaned in a dilute alkaline solution, then dried carefully, and finally dissolved in ammoniacal copper oxide solution. This solution may be obtained by oxidizing metallic copper in the presence of ammonia with a current of air ; the copper is gradually dissolved and the cuprammonium liquid is made. To the copper in the ammonia is placed a negative electro-metal, as, for example, platinum ; or an electric current may be caused to act on the metal during the oxidation. In this process the air can be replaced by pure oxygen. It is advantageous to use a solution containing at least 15 grms. (231 grains) of copper, and about ten times more of ammonia gas, per litre (0·22 gal.) : then about 45 grms. (693 grains, approximately 1½ oz.) or a little more of cellulose is dissolved for each litre (0·22 gal.) of ammoniacal copper oxide. At least eight days are necessary for the complete solution. Since the solubility of cellulose in ammoniacal copper oxide diminishes

on the one hand with a rise of temperature, and since, on the other hand, a rise of temperature is accompanied by a rapid decomposition of the cellulose, it is profitable and beneficial to keep the solvents cool in the tanks. In order to be able to utilize this solution prepared at a low temperature for the manufacture of artificial silk, it is necessary that it should be perfectly homogeneous, and to achieve this desirable condition it must be previously filtered carefully. Wool textures, guncotton, or sand may be employed for this filtration in connection with filter presses or hydro-extractors. The solution is afterwards forced through very fine openings into a precipitating liquid—*e.g.*, acetic acid—which throws down the cellulose. The cellulose thus prepared is wound on to cylinders or large bobbins which rotate in a weak bath of acetic acid. When the copper and the ammonia have been removed from the thread, the artificial silk is wound and dried at the same time by heated cylinders, or a cylinder through which a current of hot air is passed, before being wound on to spools or bobbins, while the copper and the ammonia are recovered from the acetic acid. Natural silk waste may be dissolved with the cellulose; also substances that increase the density, the lustre, or the strength of the thread may be added. However, this does not form part of the present invention.

It is quite probable that Dr. Pauly, when taking out this patent, may have had no knowledge of the previous process invented by Despeissis. As will be seen, the only new thing in Pauly's patent is the recommendation to keep the tanks for the solution as fresh as possible.

With respect to this first patent, the Leipzig court (Reichsgericht) has, however, in the meantime granted the monopoly of manufacture and sale of this artificial silk by the Pauly process to the Glanzstoff Fabriken of Elberfeld. This decision of the Leipzig court, on the interpretation of which opinions differ, is not valid in other countries; it is based only on the German law of 7th April, 1891, to declare the previous French patent null and void in Germany, seeing that the Despeissis patent has not been published in printed parts, as is done at present with lodged patents; neither had the patent been in operation in Germany at the time when the Pauly patent was presented. The latter patent claims equally elsewhere the employment of pure cellulose for the patentee's solutions at a low temperature in ammoniacal copper oxide,

although Despeissis had already said in 1890 : *The present description claims the use of pure cellulose dissolved in Schweitzer's reagent for the manufacture of a textile filament.*

We do not think that pure cellulose is absolutely indispensable when the operation is as follows. Starting with the degumming or process of preparing the cotton with the aim of cleaning it in a caustic soda bath, and putting into practice the knowledge that the addition of a fixed quantity of caustic soda to the Schweitzer's liquor facilitates considerably the solution of the cellulose, one may proceed as under : Commercial unpurified cotton is treated in a caustic lye with the intention of dissolving it immediately after without having been washed. It is sufficient to bring the concentration of the alkali to the most advantageous proportions to facilitate the solution in the ammoniacal copper oxide. The alkaline lye, which has been used for cleaning the cotton, contains greyish-brown soluble products ; the treated cotton has also a uniform greyish colour, seeing that the foreign matter only has been removed. It requires a bleaching agent, such as a solution of chlorine, to remove the colour of the constitutional impurities. We have previously spoken about the bleaching—a process which is passed over here, but which will be mentioned at the end of the manufacture of the final product of artificial silk.

The cotton that has been prepared in the alkali lye enters rapidly in solution in the ammoniacal copper oxide ; on the contrary, the constitutional impurities, and indeed all except the cellulose, remain unattacked in the solvent. A portion of the foreign matter remains in the filter press ; another portion is eliminated in the baths where precipitation and washing take place ; the remainder, as well as the constitutional impurities, is removed and displaced by the final bleaching of the hanks of artificial silk. The application of bleaching on the final product, instead of on the raw material, is of practical value only to those manufacturers who prepare the cellulose themselves.

The fibre loses from 7 to 10 per cent. of its weight during the alkaline boiling. The products that are removed by the action of the alkaline lye have been studied by Dr. E. Schunk, who has separated them as follows—

(1) Cotton wax, neutral wax melting at 80° to 86° C. (176° to 186·8° F.).

(2) Greasy acid (probably a mixture of palmitic and stearic acids).

(3) Pectic acid (an acid and gelatinous substance).

(4) Colouring matters.

The Glanzstoff Fabriken Process (German Patent No. 115,989, kl. 12, 11th January, 1900).—The solutions of copper oxide, containing more copper and less ammonia than the ordinary solutions, are prepared by cooling the metal of the receivers or cylinders which contain the copper by a current of cold air, and in reducing the temperature to from 0° to 5° C. (32° to 41° F.). This low temperature prevails all over when the copper tubes are jacketed, *i.e.*, enclosed in a second cover, and a refrigerating liquid circulates between the jacket and the tubes. The solution obtained by these means must be kept cool ; when it gets above a temperature of 5° C. (41° F.) it decomposes, and the amount of copper dissolved is reduced by about 2 to $2\frac{1}{2}$ per cent.

The Linkmeyer Process (French Patent No. 346,722).—The cotton is first plunged into a weak solution of ammoniacal copper oxide, in which the fibre softens and swells. After this preliminary treatment the cellulose dissolves very rapidly in a more concentrated solution of ammoniacal copper oxide, even at a temperature of 10° to 15° C. (50° to 59° F.), and without cooling. It has been noticed, moreover, that part of the ammonia gas is liberated during the action of dissolving the cotton ; this ammonia gas is removed from the mixing tanks by an aspirator, and may be recovered immediately in water. This operation is termed the evacuation of the pulps or the solutions. Example : 7 grms. (107·8 grains) of cleaned and bleached cellulose are immersed in 150 to 180 cu.c. (about $\frac{1}{3}$-pint) of a solution containing 9 grms. (138·6 grains) of copper and 90 grms. (1,386 grains) of ammonia per litre (0·22 gal.). The duration of the action of the solution on the cellulose must be one hour ; after this time has elapsed the cotton is taken out, pressed in order to remove the liquid, and dissolved in 100 grms. (1540 grains) of ammoniacal copper oxide containing 16 to 18 grms. (246·4 to 277·2 grains) of copper, and 250 grms. (3850 grains) of ammonia per litre (0·22 gal.). The solution is complete in a very short time, especially if to it is added a few drops of a solution of caustic soda.

The Process of the Société Anonyme Soieries Nouvelles de

Bruxelles (German Patent No. 186880).—This patent intro-
duces a new arrangement for the industrial preparation of
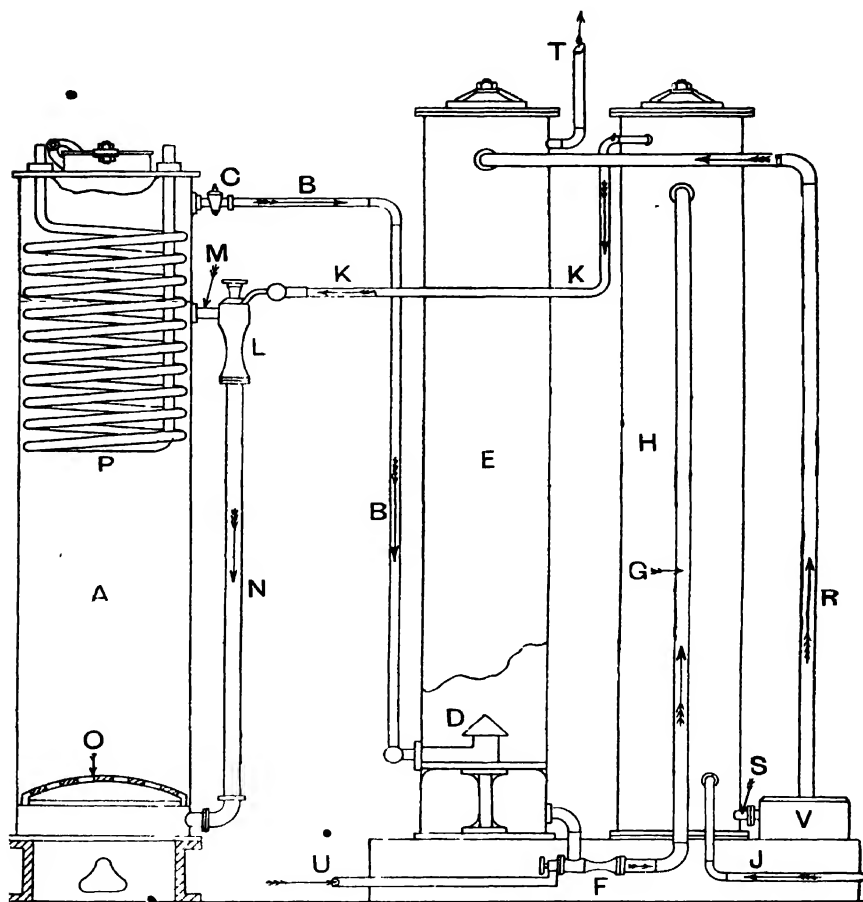ammoniacal copper oxide. It is illustrated in Fig. 54. The

Fig. 54.

air that has been used for oxidizing purposes passes out of
the top of the copper tube A and into the condenser E (coke
cylinder with pulverizer), where the ammonia gas, which has
been led in, is absorbed in water. This ammonia water is
afterwards forced out of the injector F, and through the

pipe G, into a second cylinder H, through which it falls in the form of a fine shower or spray through a current of air which enters by the pipe J and rises in the cylinder. The air becomes charged with ammonia, and is conducted by the pipes K and N, and by the large injector L, into the bottom of the copper cylinder A in order to continue the circuit. The ammoniacal copper oxide that is being made is kept in constant circulation by the aid of the injector L and the pipes M and N. In consequence of this combination the desired concentration of the solution is soon reached. B, C and D are the pipes and exit valve of the air and ammonia gas which pass from the cylinder A to the condenser E ; O is perforated iron on which the metallic copper is laid ; P is a cooling coil ; Q represents the height of the solution of ammoniacal copper oxide, a little above the exit pipe M of the solution ; R, S and V represent the parts for the circulation of the condensing water, which comes from the cylinder H to the condenser E, where it is charged with ammonia ; T is the exit pipe for the air that has been used for oxidation ; and U is a pipe through which steam passes to the injector F (this steam facilitates the liberation of the ammonia gas in the cylinder H).

La Société Générale pour la fabrication des matières plastiques à Paris has already given in the British patent, J. Chaubert (No. 14,525), a process which resembles somewhat that of the Soieries Nouvelles de Bruxelles ; it differs from it, however, in that the work is done without cooling, and without decomposition of the solution by producing the reaction in a liquid completely saturated with ammonia.

A short time ago Messrs. Wassermann & Jaegar, chemical manufacturers, Kalk, Germany, introduced a new process for obtaining a solution of ammoniacal copper oxide. Instead of metallic copper, this firm used cuprous oxide, Cu_2O, and the special preparation which they obtained is termed " cuproid." The product appears as a commercial article in the form of pulverized cuprous oxide. The following advantages accompany this process—

(1) The product " cuproid " may be recovered from chemical by-products containing copper or cuprous oxide. The details of this preparation are known only to the firm.

(2) The greatest advantages of the process result from the fact that the pulverized cuprous oxide presents the greatest possible surface to the action of the ammonia—a much greater

surface than is possible with small pieces of copper or with copper shavings which were used originally in the preparation of the ammoniacal copper oxide ; there is therefore a more rapid oxidation, the desired concentration of the liquor is obtained in a shorter time, and consequently a comparatively small quantity of air under pressure is required to produce the oxidation.   On the other hand, a smaller quantity of ammonia is taken up, seeing that the duration of the operation is considerably shortened.
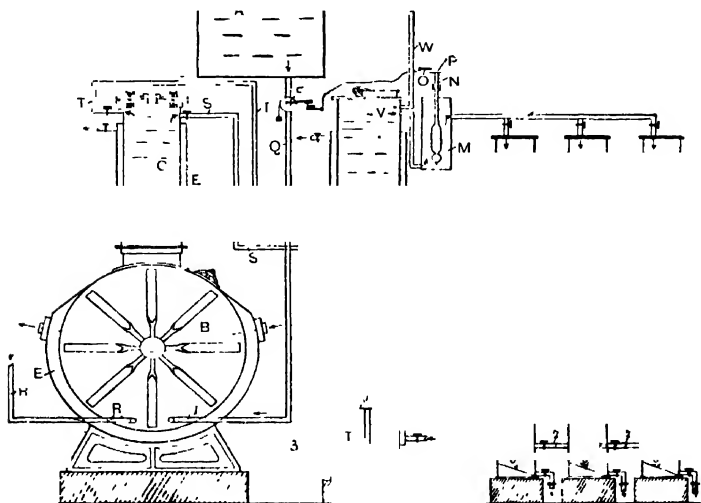
FIG. 55.

Fig. 55 illustrates an installation for the manufacture of ammoniacal copper oxide from Messrs. Wassermann and Jaegar's product, " cuproid," or pulverized cuprous oxide. Ammonia at 18° to 24° Bé. from the cistern A passes through the pipe Q and flows into the apparatus B.   This apparatus, which serves the purpose of a mixing cistern, contains the pulverized cuprous oxide, and is provided with a column C. Both mixing tank B and column C are enclosed by coverings or jackets E and E^1, and a cooling liquid circulates between these covers and the two vessels ;   this arrangement keeps

the temperature of the ammonia low during the action. Since the chemical action is much more rapid in this process than in the older process, the expense of cooling is less. The compressed air passes through the pipe R and is admitted into the tank B. through an opening near the bottom. The air rises through the mixer B, and also through column C, and, after having effected the oxidation, escapes through the outlet S. The ammonia and cuprous oxide in the mixer B are kept in motion by means of agitators, and this action, combined with the passage of the compressed air, produces an energetic oxidation, and dissolves the copper rapidly. Whilst the ammonia passes from the tank A through the regulating valve F and pipe Q to the mixer B, part of the cuprammonium liquor leaves the column C by pipe S, and enters the cylinder G where the oxidation is continued by means of the air which also leaves the column C, but by pipe T, and enters the cylinder G through the rose spray U. The object of this arrangement is to produce in the cylinder G a complete solution of the very fine particles of cuprous oxide that have been carried over into the cylinder G, or which are in suspension in the liquid. The compressed air, which traverses the pipe T, can reach only a certain height in the cylinder G through rose spray U ; the heaviest particles of cuprous oxide drop to the bottom of the cylinder at G^1. A very similar process obtains in the decanting columns H for depositing the undissolved cuprous oxide in the ammonia.—The ammoniacal copper oxide from the cylinder G passes through the pipe V and enters the three columns H through valves, and the undissolved particles are deposited in the three columns at J, J^1, and J^2. The deposit of cuproid, already highly attacked by the ammonia, is removed from time to time and added to a new solution which is being prepared in the vessels B and C.

The decanted liquid in the columns H flows through the pipe W into the tank K, and is then ready for receiving the cellulose which is to be dissolved. Column G is also provided with a jacket or cover L. The ammoniacal copper oxide, which flows from G to H through the pipe V, has to pass as shown, through vessel M, in which floats an aerometer or hydrometer N. This hydrometer N indicates the density or concentration of the cuprammonium liquor, and also checks the flow of liquid from the tank A. As soon as the ammoniacal copper oxide in the vessel M reaches the desired concentration,

the top P of the hydrometer comes in contact with O, and the
electrical contact thus formed results in opening the valve
F, which allows more ammonia to leave the tank A and to
enter the vessels B and C, where it, along with the cuproid,
is transformed into ammoniacal copper oxide. When the
concentration of the liquid is not sufficiently high, the hydro-
meter naturally descends, the electrical contact is broken,
and the valve F is closed. In this manner a continuous
preparation of the ammoniacal copper oxide is made more or
less automatically.

Wassermann and Jaegar's Process.—The inventors state
that " cuproid " or cuprous oxide dissolves rapidly, and
without any oxidation by air, when a determined quantity
of ammonium chloride is mixed first with the ammonia and
the powdered cuprous oxide added afterwards. If the mixture
be agitated for some time, a large proportion of the copper is
dissolved. The rapidity of the solution of cuproid, and the
high proportion in which it dissolves, have not been reached
for some time by any other process. The degree of solution
reaches as high as 50 grms. (770 grains) of cuproid for 100 cu.c.
(0·022 gal.) of ammonia at 24° Bé., in presence of 35 grms.
(539 grains) of ammonium chloride. The solution is effected
rapidly at the ordinary temperature, but it must be observed
that cellulose does not dissolve in this liquid at the above
temperature : when it is desired to dissolve cellulose in
ammoniacal copper oxide, the preparation must take place
at a low temperature, say, about 2° C. (35·6° F.). The
solution is advantageously prepared in the following propor-
tions : 25 grms. (385 grains) of ammonium chloride are
dissolved in the cold in 100 cu.c. (0·022 gal.) of ammonia at
24° Bé. ; to this mixture are added 25 grms. of cuprous oxide,
marked " cuproid." The whole is then stirred, and the cuprous
oxide commences to dissolve. After the copper is dissolved
there are added about 7 to 9 cu.c. of concentrated caustic
potash at a density of 25° Bé., or else a corresponding quantity
of caustic soda. The mixture is stirred again for a short
time, and afterwards left for several hours at a low tem-
perature ; a precipitate then forms, and the decanted liquid
is ready to receive the cellulose that has to be dissolved.
Cellulose will dissolve in the mixture of ammonia, ammonium
chloride, and cuprous oxide without the caustic alkali, but such
cellulose solutions are not equal in value to those which are

made with the addition of the alkalis.   Thus far we have
seen that cotton cellulose may be dissolved in ammoniacal
copper oxide by any process, but it does not follow that any
kind of cellulose can be dissolved by every process.   The
viscose works are able to use wood cellulose as raw material,
and this is cheaper than cotton cellulose.   However, in the
process that we have just described, it is possible to use
cotton cellulose or wood pulp, and to dissolve either of these
kinds in such high proportions that the textile products of
artificial silk obtained from this viscous substance have 25
per cent. more elasticity than similar products made by other
methods.   In addition to the high degree of perfection of the
products made by this progress, there is the satisfaction of
producing them at a lower net cost, and the competition
between the respective processes of viscose and copper—a
contest which appears to be to the advantage of the latter
process—urges on afresh those manufacturers who conduct
the manufacture after the cuprammonium method.   The net
cost is not only decreased with the employment of wood pulp
in place of cotton cellulose, but also by the fact that, in
comparison with the older methods, a much greater proportion
of cellulose is dissolved in the same amount of solvent ;   in
addition, the coagulation baths, which of late have for their
aim that of regenerating this cellulose in any form of artificial
textile products, have necessarily a smaller quantity of dis-
solving liquid to neutralize for a given quantity of cellulose
to coagulate.   The coagulating liquids or precipitants may, in
consequence, be less concentrated, and the tendency to weaken
the yarn is not so great ;   it is unnecessary to dwell long on the
advantages that accrue from these satisfactory conditions.

Le Procédé Prud'homme (French Patent No. 344,138).
Maurice Prud'homme intimated an interesting process for the
preparation of alkaline liquors of copper, which give concen-
trated and thread-forming or spinning solutions of cellulose,
and which improve the appearance and the touch of threads
and fabrics of cotton.

The ammoniacal solution of copper prepared by any process
whatever acquires very peculiar properties when suitable
proportions of caustic soda or caustic potash are added.   The
quantity of soda or potash that may be added without
determining the precipitate of copper sulphate, for example,
from the limpid ammoniacal solution, depends upon the

weight of copper sulphate and upon the quantity and concentration of the ammonia employed. It does not seem possible to go beyond two molecules of caustic alkali for one molecule of copper sulphate. The liquor will be composed as follows—

10 grms. (154 grains) of crystallized copper sulphate in 30 cu.c.

80 to 100 cubic centimetres of ammonia at 21° Bé.

13 grms. (200·2 grains) of potash at 36° Bé., or

9 grms. (138·6 grains) of soda at 40° Bé.

The solution of copper sulphate and ammonia may be mixed, and then the soda or potash added ; or else mix the ammonia with the soda or the potash and stir the mixture in the solution of the copper salt. But it is not necessary to precipitate the copper salt with the soda or potash, and to treat the precipitate with ammonia.

The properties of the solutions prepared as above are—

(1) They dissolve the cellulose almost instantaneously and in considerable quantity (four times the weight of the copper metal contained in the liquor). The quantity of cellulose dissolved increases as the proportion of caustic alkali approaches more nearly that of two molecules for one molecule of the copper salt. It also increases with the concentration of the ammonia, and is stronger if ammonia at 28° Bé. instead of at 21° Bé. be employed in equivalent quantity. The cellulose solutions are very homogeneous, and have a viscosity suitable for the satisfactory formation of artificial silk threads. The presence of a slight precipitate in the reaction, due to a slight excess of caustic alkali, does not hinder the solvent action, but the solutions are less viscid.

(2) The solution of the cellulose is facilitated by lowering the temperature of the solvent—the lower temperature being obtained by means of a refrigerating machine. E. de Haën, of Hanover, is credited with obtaining a lower temperature than 0° C. (32° F.) by employing caustic potash instead of caustic soda to produce his spinning solution. The extra cost of the caustic potash is counterbalanced by the saving which is effected by dispensing with the use of a refrigerator.

(3) Cotton threads immersed for one to two minutes in a solution of ammoniacal copper oxide, with the addition of a suitable proportion of caustic soda or caustic potash, swell

and appear somewhat similar to parchment. After having been washed, passed through a weak acid bath, washed a second time and dried, the fact is proved that cotton does not lose anything in length, for the temporary contraction is recovered by stretching when drying, and the fibre ultimately assumes its original dimensions. It is therefore not mercerized. In virtue of the swelling the fibre has become finer, more compact, and more lustrous, and at the same time it has acquired a particular touch, and also emits a slight rustling noise.

If the copper liquor is highly concentrated, or if it be too long in contact with the texture, the fibre is strongly attacked and tears easily, but there is no formation of oxycellulose, for blue methylene imparts a fainter stain to it than it does to the original fibre.

Other inventors have also published recipes for a solution consisting of first combining the copper and the cellulose in suitable proportions, and afterwards dissolving the mixture in ammonia and by the effect of Schweitzer's liquor which is formed by this mixture. In 1899 Drs. Bronnert, Frémery and Urban deposited a patent in which is claimed the preparation of Schweitzer's reagent by means of copper carbonate. We shall not dwell on this process, which has already been described in 1884 by De Wilde, professor in Brussels University (" Traité élémentaire de chémie générale et descriptive," tome II, p. 369).

Bernstein Process (American Patent No. 798,868).—About one ounce of copper hydroxide is mixed with two litres (0·44 gal.) of liquid ammonia, two ounces of cellulose, and about 10 per cent. of the liquid which is obtained by boiling unbleached silk. After this mixture has been allowed to cool, it is warmed slowly. In three hours the solution is complete and homogeneous, and is pressed through fine openings into acetic acid of about 80 per cent. The threads are then wound on bobbins and undergo a later treatment. After another process (American Patent No. 712756) Henry Bernstein, of Philadelphia, obtained even the same artificial silk by a simple mixture of 6·5 parts of gelatine and three parts of a liquid which is obtained by boiling unbleached silk. After having been spun, this mixture remains one hour at a temperature of 50° C. (122° F.).

In 1894 Mr. Adam Millar, of Glasgow, introduced a process

of manufacturing artificial silk by spinning lustrous threads, insoluble in water, from gelatine. The net cost of these threads was very low, but they did not appear to compete successfully with other artificial silk threads of cellulose base. It may happen, however, at some future time, that with perfected methods some such interesting efforts as those of Millar may result in the production of a low-priced and satisfactory artificial silk from gelatine alone, or perhaps from gelatine in combination with cellulose or other suitable solution.
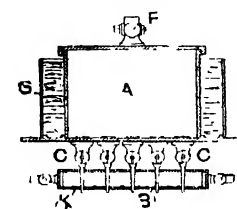
Fig. 56.   Fig. 57
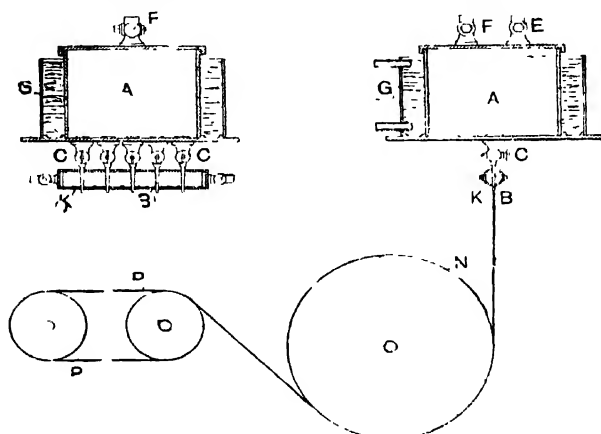
The solution of this problem does not seem impossible when we know that the Japanese have produced, with different fibres and adhesive substances of their country, a pulp from which threads as well as special kinds of paper, possessing an appearance of cloth and termed paper-fabrics, have been made. These fabrics are very supple and elastic ; they are impermeable, and can be boiled in water with little injury, and they represent types of products which have not yet been produced in Europe. It is true that such substances cannot be obtained by means of pulverizing machines, such as are used for the production of paper pulp ; neither can they be produced by boiling at high temperatures, nor by the rapid and energetic processes of bleaching, as all these operations result in a product with a superficial amount of elasticity, suppleness and silkiness. In Japan the work is performed by a skilled workman, who prepares the pulp slowly with simple

apparatus ; he then applies the substance layer after layer, exposes the product to the sun for days in order to bleach it, and leaves it for weeks to dry, after which he gives it a final polish.

To return to the Millar process in which artificial silk is made from gelatine. The process is as follows : The bleached gelatine is first dissolved in warm water, and to this solution is added bichromate of potash or some substance having a
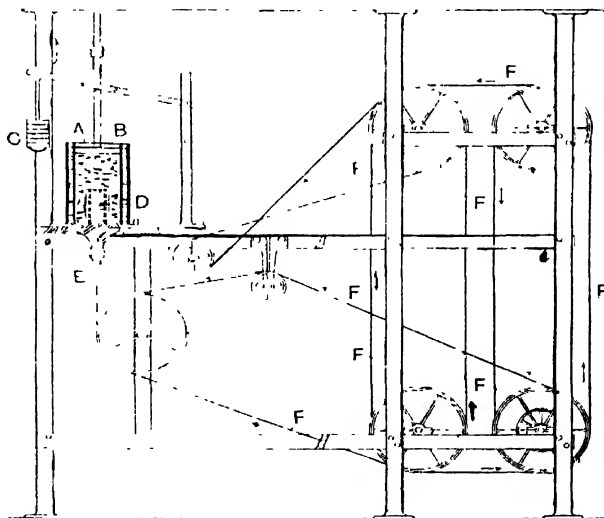
FIG. 58.

similar property, and which has for its object that of preventing the dried gelatine from re-dissolving in water. After the gelatine is dissolved, part of the water is evaporated, and the solution becomes thicker and flows through the opening E in a cylindrical reservoir A, Figs. 56 and 57, provided at the bottom with a number of valves C and attached capillary tubes B, through which the gelatinous mass is forced by air pressure passing through F ; the liquid thus emerges from the capillary tubes B in the form of threads. A double jacket G is furnished, in which warm water circulates to keep the substance in a liquid state. The same result is obtained when warm water is circulated through the canal or tube K, which encircles the extremities of the capillary tubes. In the tube K the water is kept at a constant temperature of 38° C.

(100·4° F.), as this temperature, according to the inventor, enables the threads to be formed satisfactorily. The artificial silk threads thus formed pass partially round a drum N, the speed of which is regulated to effect a slight drawing action (draft) on the filaments, and the latter, in virtue of this treatment, become finer and more silky. An endless apron P conducts the silk to a rotating bobbin or to a reel. In order to make this silk more compact and more impermeable, alum, tannin, chromic acid, gallic acid, formaldehyde, etc., are added to the gelatinous mass before the threads are formed, while glycerine, castor oil, etc., may be added to impart suppleness.

In 1897 (British Patent 2713) Adam Millar describes a new idea for the mechanical formation of silk, and the substance is not entirely artificial. The raw material employed is the silkworm itself. Millar does not allow the worm time to spin the cocoon ; he doubtless thinks that this natural method of spinning is a little slow when compared with the process which obtains in modern spinning machines. As soon as the silkworms prepared to spin their cocoons, he considered that these workers had sufficiently completed their task ; he killed them, cut them up into small pieces, and added this viscous mass to a solution of gelatine. This mixture was conveyed to a cylinder A, Fig. 58, provided at the top with a piston B actuated by a lever and weights C. The viscous liquid was forced through a filter D, which retained all membranes and other solid particles of the worm. The remainder passed out of the spinnerets E in the form of threads, and were deposited on a travelling apron F of 60 to 70 metres (65·62 to 76·55 yds.) in length. When this apron was filled, it was replaced by another one. The spinning room was kept at a temperature of 27° to 30° C. (80·6° to 86° F.) to effect a partial drying ; the aprons were then transferred to a warmer room, where the drying was completed.

CHAPTER XVIII

Precipitating Liquids : Spinning, Twisting, Removal of Copper, Washing and Drying of Threads

WE have already seen that in his patent Despeissis mentions as precipitating liquids, hydrochloric acid, sulphuric acid, acetic acid, oxalic acid, tartaric acid, citric acid, carbolic acid, alcohol, etc. Afterwards, other inventors took up patents in which they claim, in the main, the same precipitating liquids, giving precise indications as to the degrees of concentration, temperature, etc., and adding to them, for example, glycerine, or ordinary salt for the alkaline baths.

Precipitation with hydrochloric acid : The silk obtained by the use of this precipitant has a pale creamy tint, and a particular lustre which makes the fibre resemble very closely that of natural silk. However, this process is not employed in the textile industry.

The Glanzstoff Process (German Patent 125,310 kl. 29 b. of 19th October, 1900).—It is known that acids precipitate cellulose which has been dissolved in ammoniacal copper oxide by decomposing the solvent. It was not known until recently that the nature of the acid employed and its degree of concentration were of great importance with regard to their effect upon the quality of the thread. Amongst all the acids proposed, sulphuric acid may be used with advantage on account of its comparatively low price. By employing, for example, sulphuric acid of 10 to 20 per cent., a complete precipitation of cellulose results. It should be mentioned that the thread has undergone a partial decomposition ; it tears or breaks often in the spinning, and lacks solidity and softness after drying. Satisfactory precipitation is obtained when the concentration of the sulphuric acid is between 30 and 65 per cent. The best results, however, are obtained when the concentration of the sulphuric acid is 50 per cent. at the ordinary temperature. We reserve to ourselves, therefore, the right to use sulphuric acid between 40 and 65 per cent. for precipitation.

According to another process (German Patent 167,567), the Glanzstoff Fabriken Company lay claim to manufacture

cellulose products by precipitating with sulphuric acid at the outlet of the capillary tubes, and by winding the thread directly on to bobbins which rotate in a concentrated solution of caustic soda. Afterwards the artificial silk is washed, stripped of the copper, and dried under tension. We do not see how it would be possible to operate in this manner without some intermediate process, for it seems impossible for a thread which has been precipitated in sulphuric acid of 30 to 65 per cent. to be guided directly into a concentrated bath of caustic soda without losing immediately all its essential properties. The Glanzstoff Fabriken Company seems to have arranged matters by buying a little later the patent of Farbwerke de Meister Lucius et Brüning à Hoechst, which we describe later.

R. Linkmeyer's Processes (French Patents 347,960 and 350888).—This inventor also precipitates with sulphuric acid, and washes directly in caustic soda or in caustic potash ; but in this case the process is more comprehensible, seeing that Linkmeyer coagulates his threads only superficially in a weak solution of sulphuric acid of 1 to 2 per cent. ; this enables him afterwards to precipitate directly and definitely into a more concentrated solution of caustic soda or caustic potash of $10°$ to $40°$ Bé. In another more important process, Linkmeyer states that if the thread be coagulated in alkali instead of in an acid, the artificial silk obtained is no longer milky and dull when wet, but is more transparent like glass, is already lustrous before it is dried, and more solid than are those threads which are precipitated in acids. When the copper is removed from the threads and the latter washed and dried, they possess a degree of strength and of lustre which has never been reached by threads precipitated in any other of the known precipitating liquids. One interesting observation by Linkmeyer concerning the removal of copper from artificial silk threads precipitated in alkalies is, that if the copper be removed while the threads are in tension, the latter are lustrous at the time, even if they have not been dried under tension ; whereas the threads that have not been under tension during the removal of the copper, nor during the drying process, have absolutely no lustre. Therefore the lustre of these artificial silk threads may be obtained either by keeping the threads under tension while removing the copper, or during the process of drying. In práctice, however.

it is sufficient to dry the threads under tension in order to obtain a high silky reflection.

La Société Générale de la Soie Artificielle Linkmeyer returned later to precipitation by sulphuric acid (French Patent 356,402). It has been observed that a 5 per cent. solution of cellulose, from which has been removed all the ammonia gas that is liberated without promoting a premature precipitation of the cellulose, lends itself advantageously to the formation of artificial silk threads without partial decomposition of the cellulose, as is indicated in the German Patent 125,310. The copper-removal operation is then performed more rapidly, seeing that the threads contain no more than a small quantity of ammonia. According to the French Patent 352,528, Linkmeyer no longer winds the artificial silk on bobbins at the spinning frame, but receives it in a revolving cylinder in which the thread is deposited in spiral form. The removal of the copper takes place with the silk under tension by causing a supplementary tension to act on the thread (French Patent 357,837).
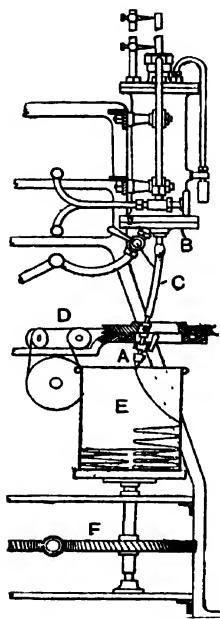
Fig. 59.

La Société Anonyme des Celluloses Planchon à Lyon has, in one operation, combined the process of adding twist to the thread with the coiling arrangement of Linkmeyer; the latter consists, as we have just stated, of depositing the thread in a rotating vessel. The twist to the thread is obtained by rotating the spinneret or capillary tube. Fig. 59 indicates the apparatus which is used by La Société Planchon; A is the capillary tube attached to the solution cylinder B by means of a flexible tube C. This capillary tube A is placed in motion by small pulleys D, and as the tube rotates, the artificial silk thread emerges from the opening, and is deposited in the rotating vessel E. The vessel E is kept in motion by the wheels F.

The Foltzer and Vermeesch Process (Belgian Patent 181,525). —According to this arrangement, the cellulose is precipitated in the form of silky and lustrous threads when a solution of

caustic soda is used as the precipitant instead of hydrochloric acid, sulphuric acid, acetic acid, oxalic acid, etc. The threads obtained by this method are characterized not only by their unaltered condition when in water, but by their much greater strength. A washable silk is therefore obtained by this process. The best results are obtained by the use of a caustic soda solution varying in strength between 35 per cent. and 45 per cent. The liberation of the cellulose by this method results, not by chemical combination of the dissolving and precipitating liquids, but by dehydration, and the cellulose thus obtained is absolutely unchanged ; hence its good qualities make it suitable for use as a textile fibre or thread.

The Process " Farbwerke vorm. Meister Lucius et Bruning a Hoechst a M." (French Patent 350,220).—The solution of cellulose is conducted through a capillary tube into an alkaline coagulating liquid at the ordinary temperature ; for example, into a caustic soda solution of 40 per cent., which precipitates the hydrocellulose. The thread thus formed is wound on to a bobbin, washed under tension—for example, in sulphuric acid of 12 per cent.—and then dried. A 4 per cent. solution of caustic soda precipitates the thread, but it appears that a more concentrated precipitating liquid results in a thread of greater strength. We think that these patents dealing with coagulation by caustic lyes—ours included—yield nothing new, seeing that it is stated, with formulae to corroborate it, in Wurtz's " Dictionnaire de Chemie " (Paris, 1870), first part (tome 1er), p. 779, that *alkalies give precipitates of cupric cellulose—that is to say, cellulose containing copper.* Besides, the corresponding Belgian Patent 180,370 of 3rd November, 1904, which has been taken advantage of by the Glanzstoff Fabriken Company of Elberfeld, has been declared void by the judgment of the Civil Tribunal of Brussels of date 4th February, 1908, and a similar patent of La Société Linkmeyer à Hal was at the same time declared void. We ourselves have lodged in Germany the Belgian Patent Foltzer and Vermeesch No. 181,525, and the improved patent, but we have been obliged to recognize the previous German Patent No. 106,043, which had a prior claim, and which we shall describe in the chapter on the manufacture of similar products.

It is generally known that alkaline coagulating liquids are more energetic when cold than at the ordinary temperature ; also that several works employ soda or potash lyes at a

temperature of 20° to 25° C. (68° to 77° F.); others conduct the operations at a temperature of 40° to 45° C. (104° to 113° F.). We have indicated that caustic soda or caustic potash even at 50° to 55° C. (122° to 131° F.) can be employed advantageously when the cellulose or wood pulp is coagulated after having been dissolved by the "cuproid" process already referred to. The firm of "Gross-Auheim," near Hanau (Germany), artificial silk manufacturers, doubtless finding itself inconvenienced by previous patents, has patented a process by means of which it arrives at the same result by heating the cellulose solution immediately before transforming it into threads; the coagulating alkaline bath may then be used at the ordinary temperature. According to the observations of some inventors, the ammonia contained in the dissolving liquid will be, by this rise of temperature, more or less free, and will be more easily liberated during precipitation. The advantages will be still more increased, and the spinning machines will be able to run much more quickly— up to 70 or 80 metres (76½ to 87½ yds.) per minute—if the cellulose solution and the coagulating liquid be heated at the same time. The effect observed by these inventors may be good from a technical point of view, but the action on the thread does not appear to possess any advantage; indeed, it is well known that the cuprammonium solution of cellulose decomposes as soon as it is heated, even when the rise of temperature is of only momentary duration, and is immediately followed by the transformation into threads. The artificial silk thus manufactured must lack the elasticity, the suppleness and the lustre of that manufactured under more favourable conditions.

E. G. Legrand, of Paris, adds diastase (which is found in cereals and tubercles) to the caustic soda coagulating bath. The advantages of these precipitating baths are as follows. A very small proportion of diastase added to the caustic lye augments considerably the precipitating effect of the liquid, and renders it more durable; it is consumed less quickly than the alkaline coagulating liquids, with or without an addition of glucose or saccharose; the resulting threads are very strong and elastic.

E. de Haën, Chemische Fabrik à Seelze, Hanover, describes a process of manufacturing artificial threads from cuprammonium cellulose solutions, in which the solution to be spun

is first suitably shaped and then passed into a coagulating bath consisting of a slightly alkaline nitre solution. The qualities of the threads are improved by adding salts, having reducing properties, to the bath, instead of nitrous salts. E. de Haën says that his artificial silk has 50 per cent. more strength and elasticity than those of better products hitherto manufactured, and that his yarns are more easily woven. E. de Haën is also the inventor of a process whereby it is possible to manufacture durable solutions for spinning artificial silk without special cooling. Hitherto this has been done by adding carbohydrates or organic acids, as in that way solutions of cellulose in copper-oxide ammonia can be prepared at the ordinary temperature, and the solutions obtained are then so durable that it is unnecessary to provide special cooling arrangements. As, however, these expensive additions must be used in fairly high percentages in order to obtain the desired object, the cost of this process is considerably increased. It has now been found that when an extract of straw is prepared with alkaline liquids, and the extract used for manufacturing the solution, the copper-oxide ammonia mixture, without cellulose as well as with cellulose, can be kept for an unlimited time, and is not harmed by exposure to a temperature of 50° C. (122° F.).

G. Guadagni, of Pavia, Italy, refers to a process which consists in adding to the ammonia contained in the agitator, after the insufflation of air has taken place, a quantity, about equal in weight to that of the cotton that is afterwards to be dissolved, of a concentrated solution of caustic soda, the density of which varies between 10° and 25° Bé. in proportion to the temperature at which the operation takes place. Then adding, in order, hydrated oxide of copper and the cotton, for the purpose of obtaining a concentrated colloidal solution which possesses a high degree of fluidity, and also possesses better properties of spinning.

Let us now see what mechanical and other processes have been proposed, or which have been applied to industrial purposes. In order to avoid the use of long circular conduits for the distribution of the solution to the different spinning frames, several new proposals have been advanced—*e.g.*, the application of telescopic pipes (a number of pipes with gradually decreased diameters, and arranged to fit each other). We mention specially the arrangement of Captain Hector

Debruxelles. French Patent No. 397,063, for the distribution of the pulp, which gives, according to a report sent to us by the inventor, in view of the decreased pressure, the best practical results in the works at Hal, Belgium, where it has been applied. Attempts have been made to replace the glass spinnerets or capillary tubes by an arrangement in which the cellulose is forced through a pipe with a perforated end piece somewhat similar to a rose spray of a watering-can, and possessing a definite number of holes. This arrangement enables the thread to receive a little twist at the spinning frame in view of facilitating the subsequent winding process.

The use of alkaline precipitating liquids instead of acid ones has necessitated some change in the construction of the
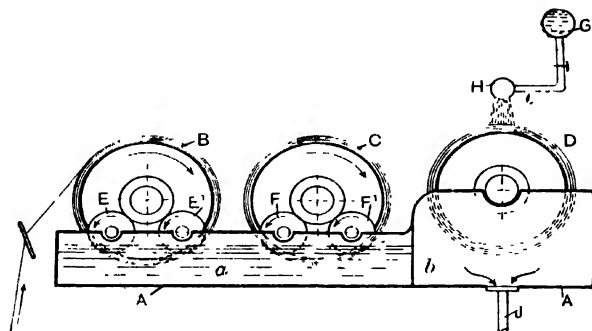
FIG. 60.

spinning frames. Thus the glass bobbins B, Fig. 60, are no longer mounted on pins or arbors, but are simply placed on rollers E, E¹, which rotate the bobbins ; the removal, as well as the manipulation, of these bobbins, is done much more quickly and easily than by the older method. The troughs A, A (in which the bobbins rotate) of the new machines are much larger, and contain two compartments a and b, and three bobbins B, C and D.

(1) The bobbin B, which is being filled with yarn.

(2) The bobbin C, which, after doffing, has been placed on the rollers F, F¹ on which it rotates, so that the thread may be coagulated through and through by rotating it a certain time in the alkaline bath. With acid precipitation this prolonged treatment is unnecessary, but it is indispensable when the operation is performed in a soda lye.

(3) The bobbin D, which previously occupied the position at present taken by C, is submitted to a washing or rapid spraying with water. The water comes from pipe G, passes through the perforated gutter or pipe H, and is sprayed on to the bobbin. The water washes off a large part of the alkaline liquor which is on the thread, and ultimately leaves the trough through waste pipe J.

The machine-maker Mertz is the inventor of the machine which bears his name, and which should replace the distributors with several capillary tubes, but we have never seen the machine in work. This machine has several capillary orifices for the liquid to emerge from in the form of threads, so that through each multiple spinneret issues a certain number of filaments which are capable of being reunited into a unique thread of silk, and of being wound on almost any kind of winding machine. A similar multiple spinneret is formed by a swelled part having a conical or pyramidic form (see Fig. 61), provided with grooves on its circumference, and terminating in capillary tubes. The capillary tubes of this spinneret have the advantage of being very easily cleaned—for example, by taking the swelled part from its cover and cleaning it by the aid of a brush or other convenient article ; or, again, by simply exerting a pressure on the outside terminal point of the swelled part so as to force it inside, and thus enable the liquid under pressure to escape in large quantities through the grooves of the swelled part, and thus to lead away the impurities.

Fig. 61.

The cleaning of the spinnerets, however, is seldom required when the apparatus is provided with longitudinal trunconic grooves and with ring-shaped necks at the periphery of the swelled part ; these grooves and necks allow the impurities to accumulate without entering easily into the terminal capillary conduits of the spinnerets. Although the Mertz capillary tube has not been a commercial success, other later inventors have used the idea. They have, however, abolished the simple capillary tubes, and replaced them by a series of branch pipes and distributors in order to employ a number of capillary tubes as a group, and arranged as a rose distributor. These are preferably made of glass, and the small openings
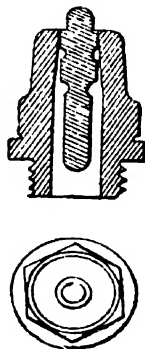
of the capillary tubes are made during the moulding of the
glass by inserting very fine iron wires, which are withdrawn
afterwards, or else corroded by means of an acid.   According
to C. Woegerer, these capillary tubes may be prepared in the
following manner : Near the circumference of the end of a
glass rod, which is softened by heat, a number of fine metallic
wires are inserted parallel to the sides of the glass rod ; these
wires are thus incorporated with the glass after the latter
has become cold.   Sections are then cut from the combined
rod of glass and metallic wires, and the metal removed by
an acid.   Afterwards each thin section, perforated near its
periphery, is mounted into the end of a pipe or corresponding
article, and a thoroughly practical rose capillary tube, with
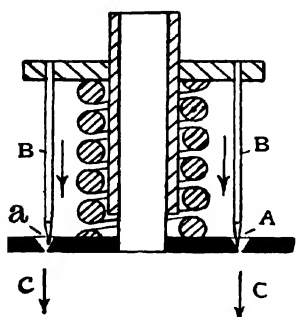absolute regularity in the size of the holes, is secured.

Fig. 62.

The American Patent No. 858,648
proposes to make the capillary
tubes of ebonite ; while, on the
other hand, it has been suggested
that the capillaries should be made
with adjustable openings, somewhat
as illustrated in Fig. 62.   Into the
capillary openings A, fine-pointed
rods B, mounted on an adjustable
disc, may be introduced to a greater
or less extent in order to change the
sectional area of the opening ; the
viscous jet which forms the thread
is forced through the openings in
the direction of the arrows C, C (German Patent No. 221572).

Alexandre Berstein, of Berlin, employed two discs, one
superposed on the other, and both containing a series of holes.
The two discs could be so placed that the holes in one disc
were immediately above the holes in the other, in which case
a maximum circular opening was presented to the viscous
fluid ; on the other hand, one disc could be moved through a
very small angle, in which case a smaller but crescent-shaped
opening would result, and a finer filament be obtained.   We
may also mention the arrangement of La Soie Artificielle de
Basècles, described in the French Patent No. 410,267, which
consists in mounting adjustable capillary tubes on a dis-
tributor ; the solution can pass only when the capillary tube
is inclined at a certain angle to the distributing pipe.

Other factories have employed advantageously for some
time a simple arrangement which is more or less similar to
that of La Société de Basècles. The apparatus is illustrated
in Fig. 63, where A is the multiple capillary tube which is
hinged to the distributor B. When the machine is at rest,
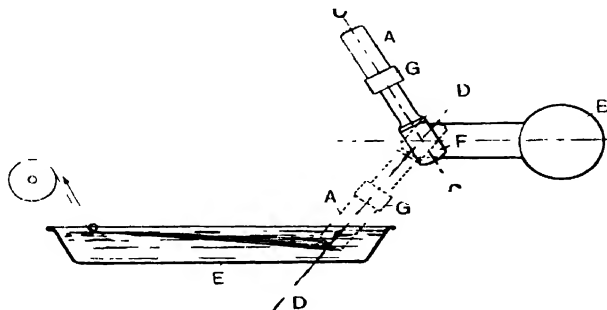
Fig. 63.

the capillary tube is in the position indicated by solid lines,
and the solution is shut off by the tap F : it is only when the
tube reaches the dotted position, with centre D D, that the
viscous liquid can emerge through the various openings of
the capillary tube into the bath E, from which it passes as
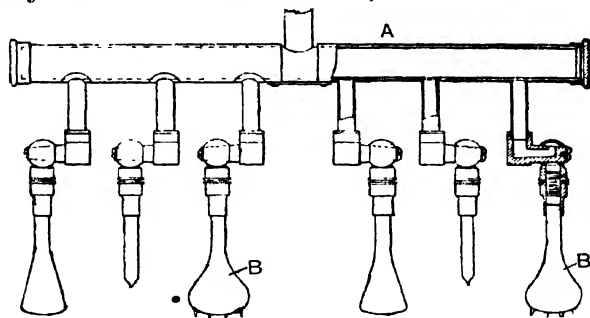
Fig. 64.

indicated by the arrow. A filter, secured by two indiarubber
washers, is fixed in the sleeve G for the purpose of arresting
foreign matter and imperfectly mixed solution.
    Fig. 64 illustrates another arrangement of a distributor A
with hinged multiple spinnerets B.
    According to an English patent (No. 4080, 1911), Oskar
Müller and Messrs. Franke Frères, of Chemnitz, introduce a
swelled or enlarged part in the pipe between the conduit

pipe and the capillary tubes. The inventors consider that this enlarged part will prevent differences in pressure, and, in consequence, the threads will be more regular in thickness. The same firm has also introduced quite a number of improvements to their machines for spinning artificial silk, but it would occupy too much space to give all the details here. We illustrate, however, the spinning machine of Messrs. Müller and Franke in Fig. 65. The solution coming from
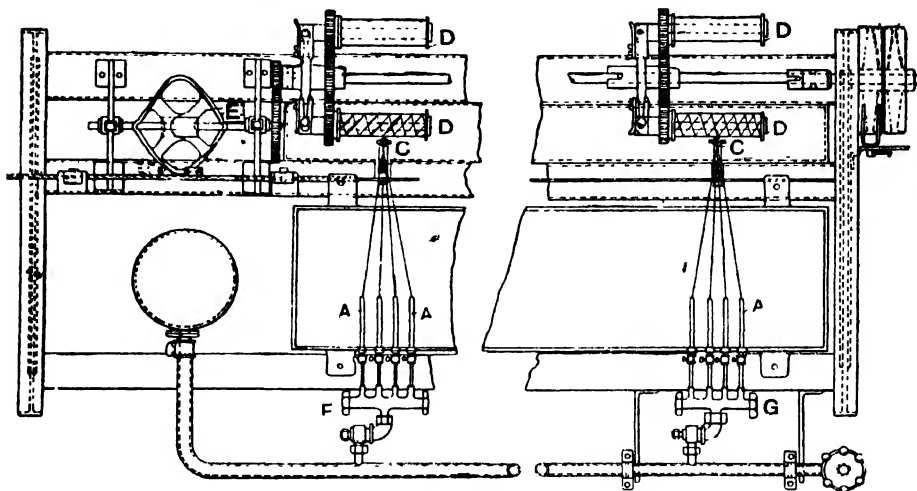
Fig 65.

the distributors F and G emerges from each capillary tube A A in the form of a thread ; these threads pass through a thread guide C, where they receive a slight twist, and the compound thread is then wound on to bobbins D. These bobbins are driven, as shown, by toothed gearing. The thread guide receives its movement from a cam E, and a regular cross-wind effect is obtained.

Fig. 66 is a section of a spinning machine used by R. W. Strehlenert, of Stockholm, for spinning nitro-cellulose. The special aim of this machine is to conduct the threads automatically from the capillary tubes, and through the coagulating bath, up to the winding process ; since the machine is designed to carry forward even those threads which break at the capillary tubes, the arrangement dispenses in a great part, with the use of piecers. Moreover, since at the same time the threads receive a slight twist, those filaments which break

are caught and entwined by the neighbouring filaments, and hence waste is reduced to a minimum.

The solution is kept under pressure in a tank, not represented in the figure, and is conveyed to the machine through the pipe K. It first enters into a rotating pipe F, which is provided with two or four branches L. These branch pipes are bent as shown, and lengthened by parts B ; the latter carry at their extremities the capillary plates A, through the
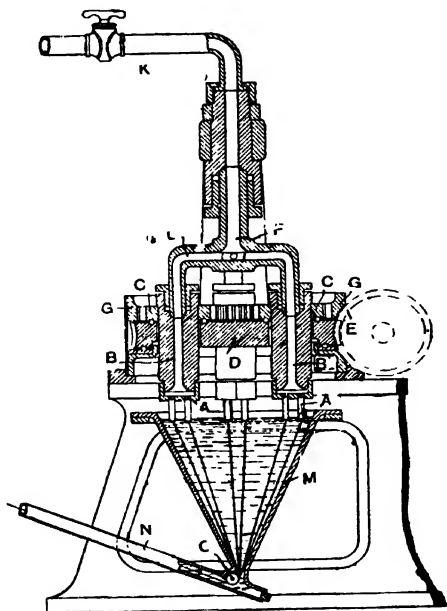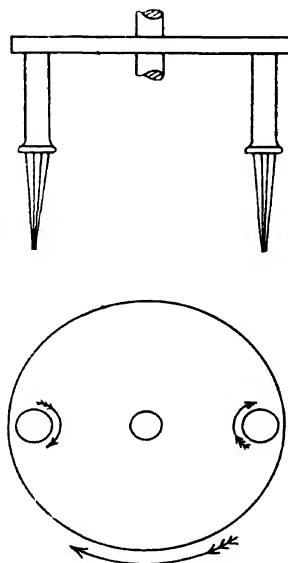
FIG. 66. FIG. 67.

openings of each of which four threads pass. The supports B carry toothed wheels C, which are rotated by wheel D, the latter being driven by wheel E. Toothed wheels C also gear with the interior teeth of crown wheel G, so that the tubes B, and consequently the capillary tubes or spinnerets A, rotate first in virtue of the gearing through D and E, and they also receive a circular motion in virtue of the motion of F. Hence the threads from each group emerging from each capillary plate A are rotated so as to receive a slight twist amongst themselves, and at the same time the four twisted

threads from each group are united and twisted with the other groups coming from the remainder of the capillary plates A. The arrangement is diagrammatically shown in Fig. 67. The coagulating liquid is in the funnel-shaped receiver M, Fig. 66 ; it enters near the top and flows downwards, with a tendency to lead the threads to the guide roller O and the delivery pipe N. The pipe N leads into a little tank, not shown, in which rotates the bobbin upon which the twisted thread is wound.

The direction followed by the jet of coagulating liquid at the top of the funnel must coincide with the direction in which
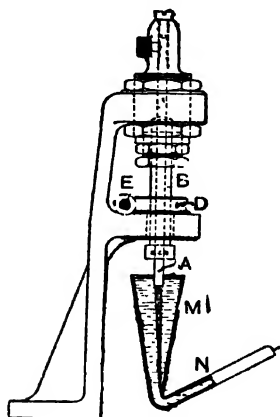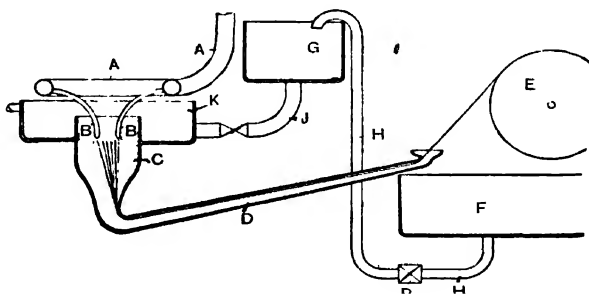
Fig. 68.   Fig. 69.

the threads are rotating, and the jet should lead the threads in such a way that those which break, and which show a tendency to escape from the group, may be forced into the group, and thus become joined to the unbroken ones.

Strehlenert later simplified his arrangement as shown in Fig. 68 by employing only one multiple spinneret A. This spinneret dips into a funnel M N, and receives its circular motion through a worm-wheel D and a worm E. The solution arrives under pressure by the spinneret carrier B. In an American patent (No. 1022097) C. R. Linkmeyer describes a spinning apparatus adapted for the cuprammonium process, and capable of employing spinnerets with large openings ; the thread is drawn to the desired degree of fineness between the capillary tube and the winding bobbin. The solution, under pressure as usual, is fed to the machine through pipe A, Fig. 69, and

passes through the capillary tubes B, each of which dips into the funnel C. This funnel contains the coagulating liquid, is open at the top, and its lower part D is bent as shown ; the thread emerges from the mouth of the pipe D, and immediately comes in contact with the winding bobbin E. The bore of the capillary tube is from 0·35 to 0·40 mm. in diameter, and the thread is drawn through the coagulating bath, which is composed of 100 litres (22 gals.) of water for 1 litre (0·22 gal.) of caustic soda lye of 38° Bé., and of 4 kgs. (8·816 lbs.) of common salt. This liquid is supplied to the tank G from the tank F by the pipe H and the pump P ;
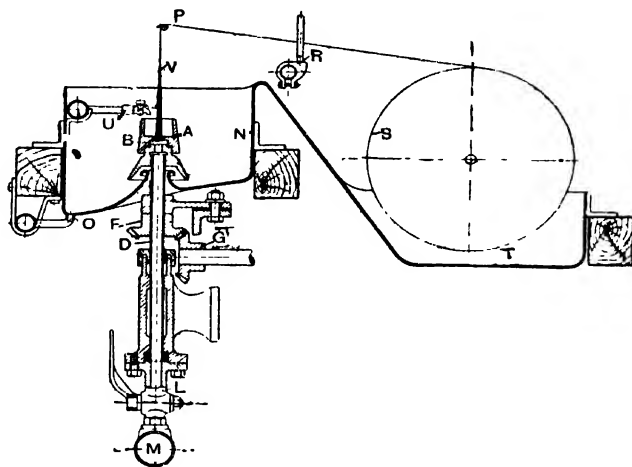
FIG. 70.

and from tank G the liquid is conveyed through the pipe J to the funnel B. The surface speed of the winding bobbin E is 35 metres (38·28 yds.) per minute. Coagulating baths of sulphuric acid and of glycerine may be employed instead of the alkaline lyes. Linkmeyer states that by this method he is able to spin from thicker solutions containing as much as 15 per cent. of cellulose in solution.

Another spinning machine by C. R. Linkmeyer, and one by means of which it is possible to spin and to twist artificial silk simultaneously, is illustrated in Fig. 70. A spinneret B is fixed in a hollow spindle D, and the latter is rotated by means of bevel wheels F and G. The solution under pressure is supplied through the pipe M and valve L, and flows through

the hollow spindle D ; after the solution has passed through the coagulating liquid, it is carried over thread guides P and R, and is finally wound on the bobbin S, which is partially immersed in the trough T. The coagulating liquid is admitted by pipe and valve U, and drops into a little cup-shaped receptacle A fixed in the top B of the spindle D, and therefore all the parts rotate together. This arrangement is very simple, and permits of the spinnerets being changed easily. The filaments that break are thrown into the bath N, which also receives the spent coagulating liquid. The latter flows away through pipe O into a tank, where the bath is regenerated in order to be employed again.

C. A. Granquist, of Stockholm, has introduced a very simple apparatus by which he imparts a certain amount of twist to the threads. The threads to be twisted are conducted obliquely on the rapidly rotating cylinders A, A, Fig. 71. In order to obtain the twist, the thread C C slides between two thread guides B, B, one of which is before and the other behind the cylinder A, but not in the same line. A very regular thread may also be produced by
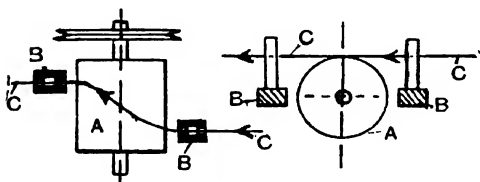
Fig. 71.

having a thick unbent capillary tube of a few centimetres placed above a precipitating liquid. The solution flows through this tube, and gets thinner or stretches itself out in some way proportionately to the height through which it falls. The thread of solution is found precipitated in the bath in the form of an artificial silk thread, and is then wound on to a bobbin in the well-known manner.

Charles Fred Topham, of London, is the inventor of the spinning mechanism illustrated in Figs. 72, 73 and 74. This machine spins the thread, imparts twist, and delivers the product in the form of cakes. A solution of any kind of cellulose reaches the apparatus by pipe A, Figs. 72 and 73, as far as the regulating valve B, and then passes through a horizontal opening and into the canal C, Fig. 74, enclosed in a bottle filter D. When the solution leaves the canal C it falls on to a filter E, say, of cotton, supported by a cloth F or a metallic tissue. The pipe C and the filter E are enclosed,

as shown, by the outer chamber. The bottom of the latter is screwed down to the part G, and the top is joined to a pipe H in the spinneret J. The filtered solution makes its way through the pipe H, and the threads emerge into the coagulating bath K, Fig. 72. From this bath they pass over a bobbin L,
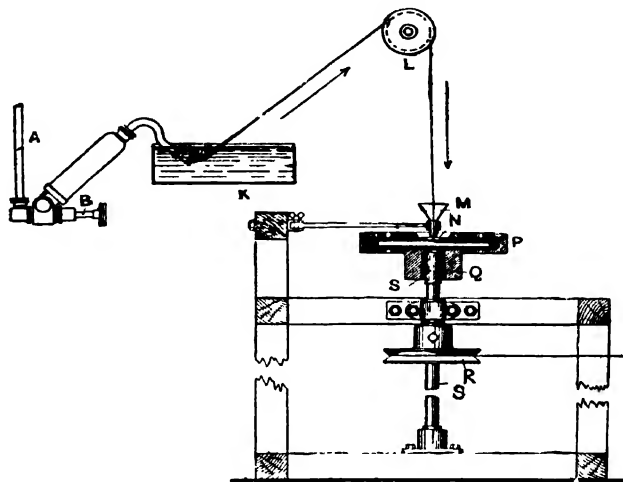
FIG 72.

drop into the funnel M N, and are then under the influence of a rapidly revolving drum P Q. By this circular movement of the drum the filaments of artificial silk are twisted together, and, as a result of the centrifugal force, the threads thus formed are deposited in the form of hanks on the inner circumference of the drum P, which receives its movement from the grooved pulley R on shaft S. Of two other improvements of the apparatus, one consists of impart-

FIG. 73.

ing to the drum P Q an up-and-down movement in addition to its rotary one, so that the threads of the cakes are cross-reeled. The other improvement is the method adopted for fixing the pipe H, Fig. 74, to the neck T of the bottle D, by lengthening and tapering the end U. By this arrangement the solution passes through U in the pipe H, whilst the
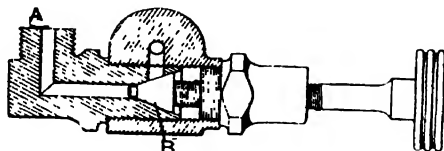
air bubbles, which may still be in the solution, and which always have a tendency to occupy the highest part of the bottle D, slide into the gap between the extension part U of the tube and the neck of the bottle.   These air bubbles escape as soon as the neck-piece J is unscrewed.

In that section dealing with the description of the works it is shown how the artificial silk on bobbins is washed by
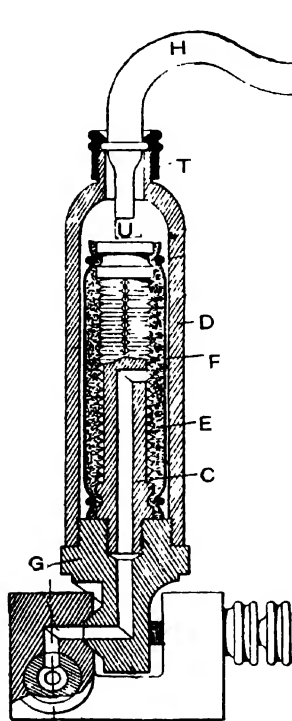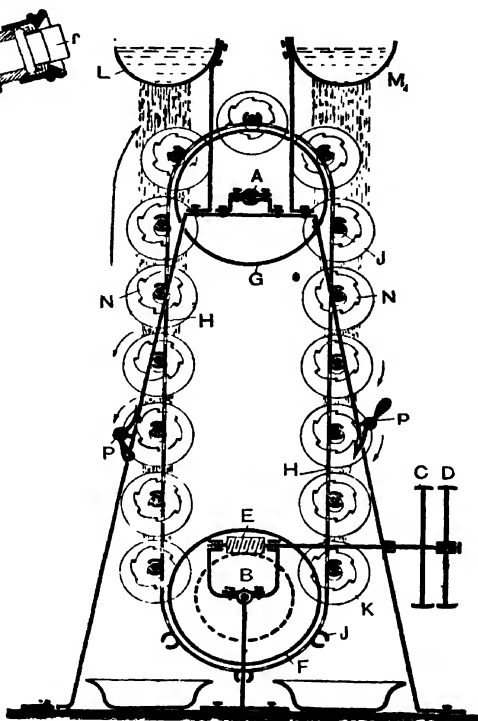
FIG. 74.   FIG. 75.

means of perforated gutters, Figs. 35 and 36. Linkmeyer has proposed to spin on perforated bobbins, and to cause a current of air or of steam to enter between the layers, and thus to draw away part of the ammonia gas, and to obtain in consequence a rapid removal of the copper.

Foltzer's Washing Machine.—We have attempted to replace the method of washing by means of perforated gutters by a double and continuous operation as illustrated in Fig. 75.

The bobbins of artificial silk or similar products charged with the precipitating liquid or other substances, which it is necessary to remove, are placed in suitable supports attached to an endless chain H. This endless chain is driven in the ordinary way by pulleys C and D, worm E, and worm-wheel on shaft B ; sprocket or similar wheels F and G carry the chain H round slowly and continuously in a clockwise direction when the belt is on the fast pulley C. The washing solution drips from the perforated chambers L and M on to the bobbins, and in order that each part of the circumference of the bobbin may come in contact with the falling liquid, the cylinders or bobbins are automatically turned one-sixth of a revolution counter-clockwise each time that the ratchet wheels N come in contact with either of the pawls P.

Another method of washing and removal of copper, which gives equally good results, is illustrated in Fig. 32, p. 67. The bobbins are placed in a bank arranged in tiers as shown, and the cart containing the bobbins is simply placed under a number of perforated gutters corresponding to the number of rows of bobbins. After the bobbins have been washed, they are wheeled under another set of perforated gutters of different baths, and so on. This method reduces very considerably the handling of the bobbins.

The bobbins may also be washed and the copper removed by simply placing them into a tank or cistern in which a current of air is introduced to agitate the copper-removal liquid or the washing liquid.

From the beginning of the manufacture of artificial silk by the cuprammonium process, attempts have been made to dispense with the use of glass bobbins or cylinders in the spinning process. We have tried to achieve this end by mounting a series of little bobbins on spindles in a revolving frame, and arranged in front of the capillary tube distributor, and near the position occupied by the glass bobbin. Each bobbin in turn was placed into the washing bath, where it was rotated by means of a friction drum in order to wind on the thread. After each evolation the thread is simply drawn on by the new bobbin in rotation. By this arrangement it is possible to avoid the intermediate process of reeling, and the little bobbins are taken direct to the twisting department. The practical result of this installation has not proved satisfactory. However, La Société Ital. della Seta Artificielle

of Pavia spins ammoniacal solution of copper oxide on little wooden bobbins covered with celluloid.

It is an easy matter to dispense with the glass bobbins by spinning on to reels. This permits of the process of copper removal, as well as the processes of washing and drying the threads, being carried out directly. However, the winding of the threads on to the reels is not so regular as winding on to bobbins, and the threads are more difficult to tie.

Whilst the Glanzstoff Fabriken, of Germany, practise natural drying and without supplementary tension on the glass bobbins, Rudolf Pawlikowski, of Goerlitz, thinks that it is an advantage during the drying process to impart a supplementary tension to the threads that are wound on to bobbins, and for this purpose he has used a special type of bobbin, illustrated in Fig. 76. A special cylinder A is surrounded by a flexible band B, which, during the process of winding the silk at the spinning frame, is kept at a comparatively small diameter by means of the projecting inner edges of parts C; the latter are screwed on to the ends of the cylinder A. When the bobbins filled with silk are ready for drying, the parts C
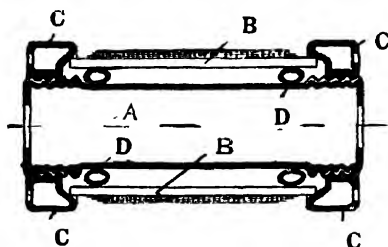
FIG. 76.

are partially unscrewed until the extreme projecting inner parts leave the edges of the flexible band B. When this occurs, the latter naturally expands slightly in consequence of the release of pressure upon the compressed indiarubber rings D, or springs. The inventor claims to obtain by this method a very lustrous surface on the artificial silk, and it is quite possible that he has done so.

Benno Borzykowski, of the Boroid Company, London, according to a German patent, obtains the same effect, and in addition very flexible products, in a more simple manner. During the time that the silk is being wound on to the bobbin, he imparts a degree of tension to the thread by means of two rollers which rotate at different speeds. The surface speed of the first roller is the same as the speed at which the thread leaves the capillary tube, but the surface speed of the second roller is slightly greater, and, consequently, a slight tension is imparted to the thread during the winding process.

Fig. 77 represents the spinning machine of Borzykowski. The new arrangement in this machine is such that two or more tiers of bobbins P are employed, an arrangement which clearly permits of the same production in much less space—little more than half. The distributing pipe C supplies the solution to all the capillary tubes D which, as usual, dip into the coagulating bath B. The artificial silk threads E leave the mouths of the spinnerets D, and are conducted, some to the upper row and some to the lower row of those bobbins P which are opposite to the mouths of the spinnerets. All the bobbins P are mounted on spindles N and rotate in a washing
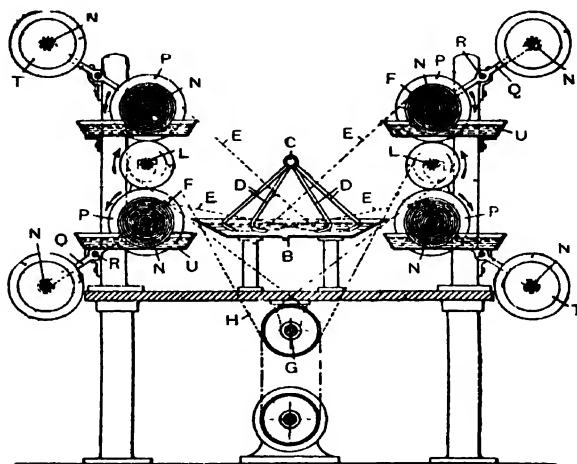
FIG. 77.

bath U. The bobbins P are driven by frictional contact with drums L, which receive their motion from the main transmission pulley G and strap H. A rod Q, pivoted at R, is arranged to support a bobbin at each end, so that while the silk F is being wound on one bobbin, the full bobbin at T may be removed and replaced by an empty one. The arrangement of the various parts of the machine is very simple, and it gives good practical results.

La Société Bouiller et Lafais, of Paris, employs a machine somewhat similar to that illustrated in Fig. 78 for the spinning of nitro-cellulose. The artificial silk threads emerge from a series of capillary tubes A, and pass in front of two coils of

steampipes B, the heat from which dries the threads.   All the threads are joined together by a collecting thread guide C, from which the group in the form of a single thread is guided by another thread guide on to either the bobbin D or bobbin E, according to which is empty or partially filled.   Electric radiators may be used instead of the steampipes, and the drying temperature is about 40° C. (104° F.).
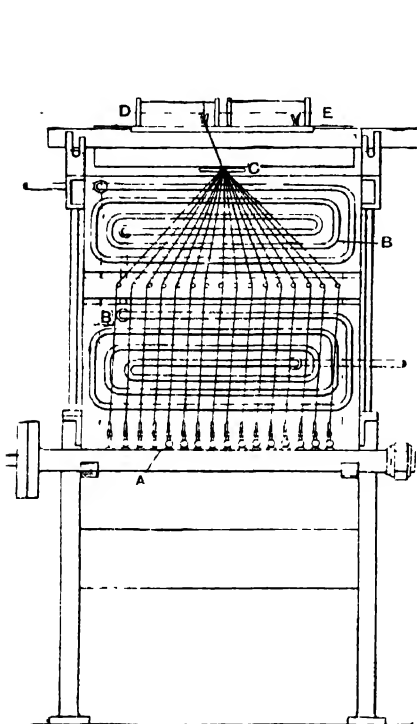
FIG. 78.
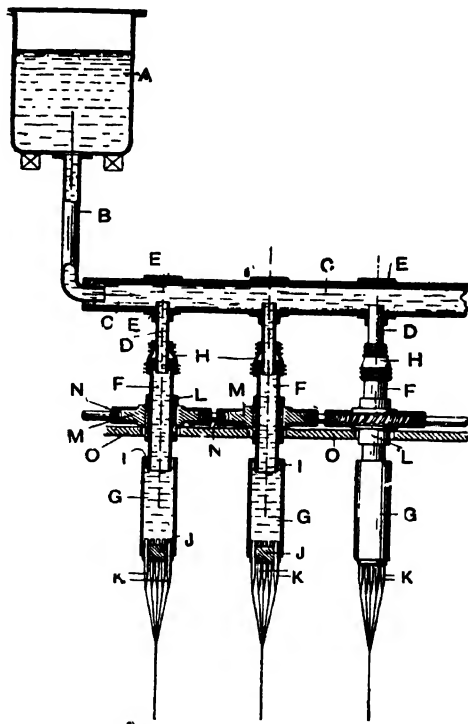
FIG. 79.

In the French Patent 434,869, G. Cahen describes an interesting apparatus for spinning artificial silk in natural air and without any supplementary pressure.   The solution of cellulose is kept in the tank A,   Fig. 79, and conveyed by pipe B to the main distributing pipe C.   Holes E are bored in pipe C, and through these holes pipes D are adjusted so that they may be rotated to impart some twist to the filaments. Pipes D are screwed into longer pipes F, and the latter into

sleeves G. The pipes must naturally fit tightly at points H and I, so that there will be no waste or loss of solution. The pieces J, fixed in the sleeves G, are provided with capillary tubes K. Worm-wheels L, M, fixed on F, are operated by worm N, and the circular motion which results imparts the desired degree of twist to the threads as they emerge from the capillary tubes K. The whole system is carried by the rail O. This system would be specially applicable for the Chardonnet process.

Quite a number of different arrangements have been patented. Some propose to allow the threads to fall into a fixed receiver, which might eventually be a perforated one to permit of the operations of copper removal and washing being carried out before reeling the thread. Others impart a movement to the receiver or cylinder to obtain a twist on the thread, the latter being laid on in regular layers. We have already had occasion to speak of the spinning machine of La Société des Celluloses Planchon à Lyons, and we now give a more or less detailed description of the spinning machine of Messrs. Courtaulds, Ltd., London. This machine spins and twists at the same time the viscose silks in the works of Messrs. Courtaulds, Ltd., and it shows a considerable advance in the artificial silk industry. Fig. 80 shows a section of a multiple spinneret mounted on a spindle and arranged to be put into motion. The same figure also indicates the part where the viscose arrives, the arrangement and the disposition of the driving of the spindles and of the spinnerets. Fig. 81 represents a sectional view of the pump and the spindle, as well as the method by which the different parts are joined together and fixed on the framework and supports. Fig. 82 is a section of the driving arrangement of the multiple spinneret supports.

On the framework 1 are fixed the supports 3, which carry the main shaft 4 and the friction pulleys 5—one friction pulley for each spindle and spinneret. On the framework 1 are other brackets 6 for carrying arbor 7, upon which is fixed the worm 8. Worm 9 drives worm-wheel 27, which operates pump 16. By means of gearing, which is not shown in the figures, the arbor 7 and the worm 9 may be governed and put in motion from the main shaft 4. Pipe 10 is the viscose distribution pipe. Lengthening brackets 11, fixed to brackets 6, Figs. 80 and 81, support the bearing blocks of the framework

12, 13, 14 and 15. This framework can turn around these bearing blocks, and one of the arms 13 of the framework is perforated and devoted to the passage of the viscose. The viscose flows through pump 16 into filter 17, Fig. 81, is driven forward through tube 31, and then through tube 32 into the
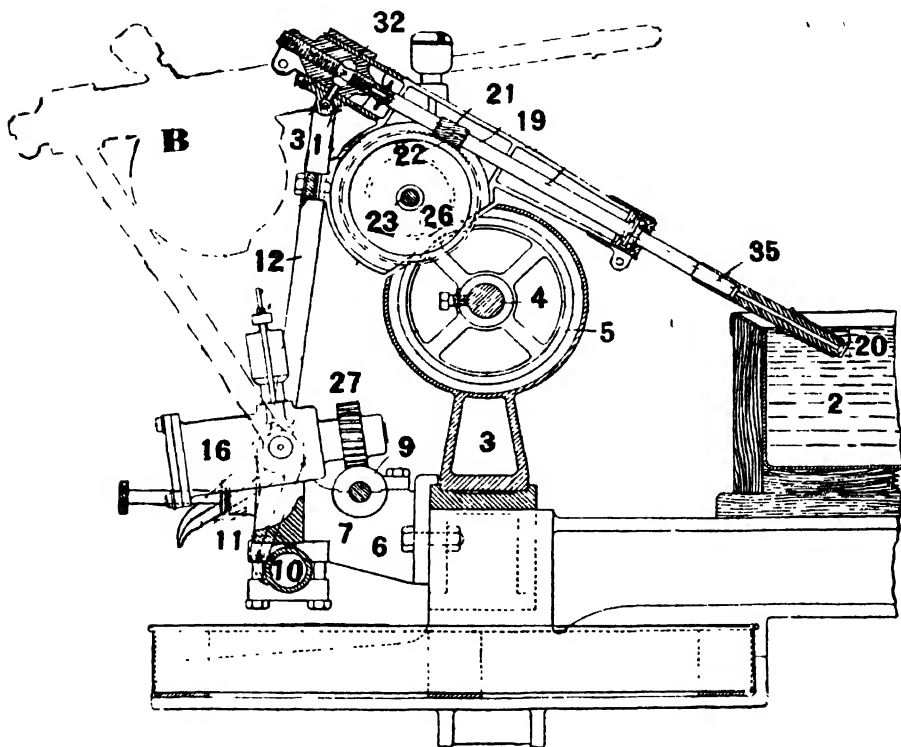
FIG. 80.

perforated bearing block of spindle 19, Fig. 80, and finally through the openings 20 of the spinnerets 35 into the coagulating bath 2. The rotation of the spindle 19 is usually accomplished by means of a worm 21 fixed on spindle 19, and a corresponding worm-wheel 22 fixed on arbor 23. On worm wheel 22 is fixed a friction pulley 26 which is applied to friction pulley 5 when the spinneret 20 dips into the

coagulating bath 2. When the pump 16 is placed into action, it is necessary that its position should be such that worm-wheel 27 will be in gear with its worm 9 ; the viscose from the distribution pipe 10 passes then through channels 28 and 29, Fig. 81, to the pumps 16, and is forced through the opening 30, filter 17, channels 31 and 32, into the interior of the perforated spindle 19.

Fig. 80 shows the method of mounting the spindle 19 in its case ; it also shows the simple and practical method of fixing all the apparatus, any single piece of which may be connected or disconnected or replaced by a simple movement of the hand. When the apparatus is out of action at rest, the spindle 19 and capillary tubes, as well as the framework which supports them, occupy the dotted position B ; the gearing is arranged so that the pump 16 might still act at the time when the spindle and spinneret are in the dotted positions— an operation that results in forcing out air bubbles which might otherwise be found in the viscose solution before its transformation into threads of artificial silk.
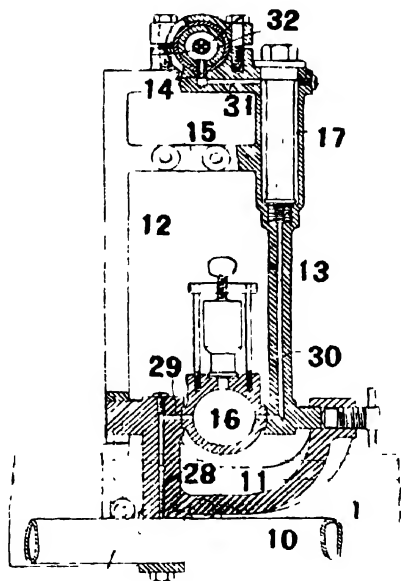
Ch. C. Leclaire describes an apparatus for spinning which

Fig. 81.

is so arranged that the coagulation bath, in which is formed the viscose or other artificial silk thread, may be rotated in the same direction and at the same speed as the capillary tube which dips into the bath. By this combination the coagulation bath may be considered as stationary with regard to the threads in process of formation ; the threads are formed, indeed, under pretty much the same conditions as would obtain if both the capillary tubes and the coagulation bath were fixtures. It is natural to expect that the filaments of silk thus formed will be less fatigued during the operations

of spinning and twisting than they would be with a stationary coagulating bath and rotating capillary tubes.

Fig. 83 shows that the spinneret is fixed on a spindle E that is rotated by frictional contact between parts D and A. The spindle can be placed in and out of gear with the driving part A by means of the pin H, fork J, lever K, and the other arm of lever K not completely shown in the figure. The spinneret P is fixed to the top of the spindle E, and the coagulating bath G is also secured to the spindle so that all rotate in unison. The coagulating liquid flows through pipe
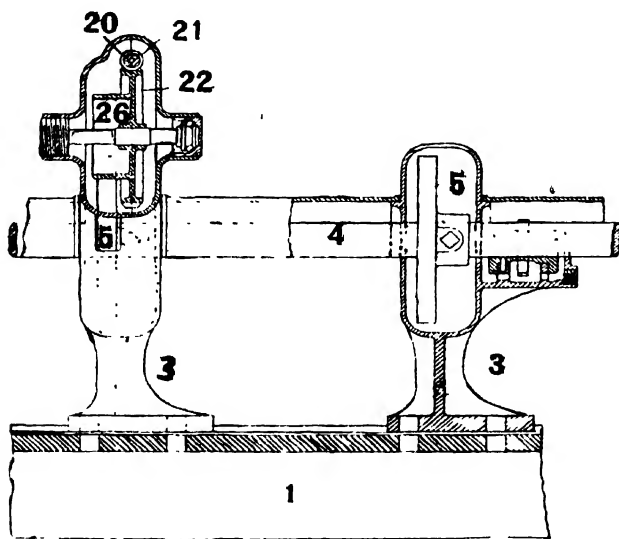
Fɪɢ. 82.

R and the interior channel N of the perforated spindle E, and finally into the coagulating bath 'G through an opening in the centre of the spinneret P. This spinneret P, fixed, as stated, on spindle E, consists of capillary openings situated on the circumference of the disc which forms the spinneret, whilst the coagulating liquid, as we have just stated, flows through the centre of the same spinneret. By this arrangement, the liquid, due to centrifugal force, crosses the jets O from the spinneret P, and escapes on the circumference of the spinneret, causing an energetic precipitation. The viscous substance to spin is forced through the pipe U up channel S,

into the bell-shaped opening V and the spinneret P. The bath G is partially covered with the lid W, an opening X being left in the centre for the free travel of the threads O. The
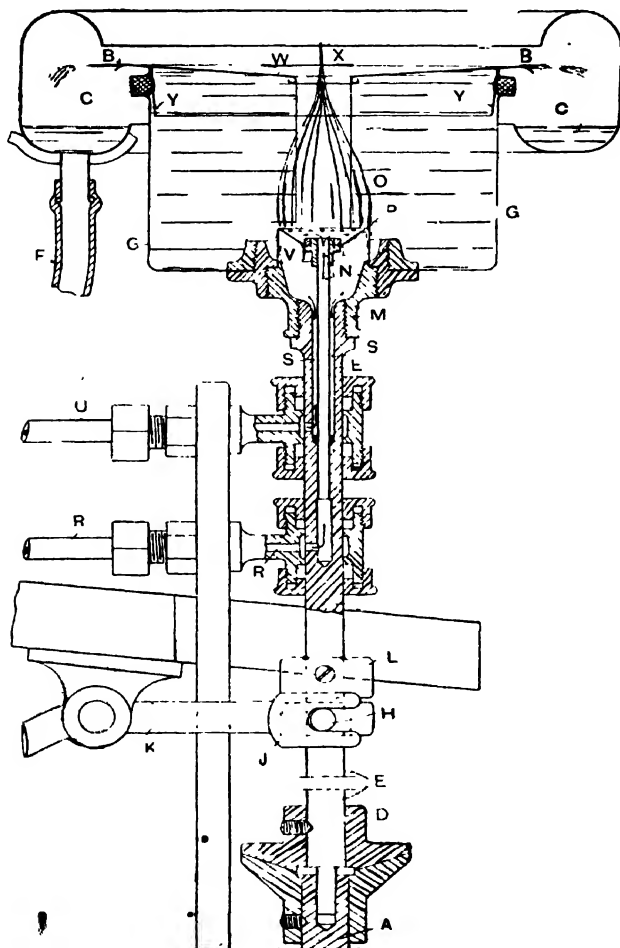
FIG. 83.

edge of the cover W extends beyond the edge of the bath, and thus provides a means of conveying any waste liquid over the edge B and into the fixed channel C, from which it

returns through pipe F to the store tank of coagulating liquid, to be placed again in circulation through pipe R.

A considerable improvement in the method of spinning artificial silk is that embodied in the invention of La Société de la Viscose française. Fig. 84 is a section of this improved arrangement. The particular function of this mechanism is that of imparting a twist to the thread as it is being spun. This is done by imparting a rotary movement to the spinneret G fixed on a special frame. The solution is led to the spinneret by a central pipe A, and passes through the opening C, the size of which is regulated by screw B; it then flows through tube D, passes through filter E, then through pipe F into the spinneret G. The apparatus is jointed along the axes x and y, and is held in the former position by a screw attached to the milled head H, and in the second position by a nut J. By this arrangement it is possible to place the spinneret immediately into the precipitation bath, or to replace any part by a turn of the hand. The pipe F, which carries the spinneret G, is rotated in cylinder K. The artificial silk threads L, which emerge from the spinneret G, pass into the coagulation bath, and under a guide roller M. and are afterwards wound on to a bobbin, or else reeled into hanks (these parts are not shown in the figure). A left-handed screw N and a right-handed screw P on the pipe F Q serve to force or press the solution towards the middle of the pipe. The circular movement of the spinneret communicated from
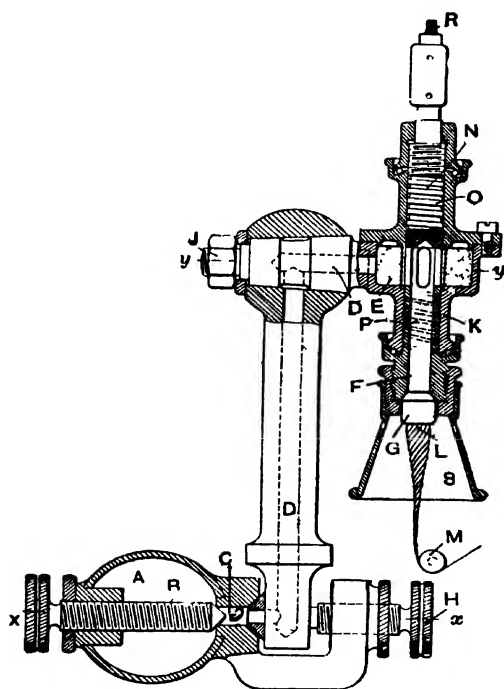
FIG. 84.

point R twists the various filaments coincident with their formation. A sort of funnel or cone shaped projection S guides the rotating threads into the coagulating bath as they emerge from the spinneret. The rotating spinneret and the funnel dip into the coagulating liquid. This provision minimizes the number of breakages.

La Viscose française have also introduced an apparatus that enables them to subject the hanks under tension to the action of an acid or other liquid having for its object that
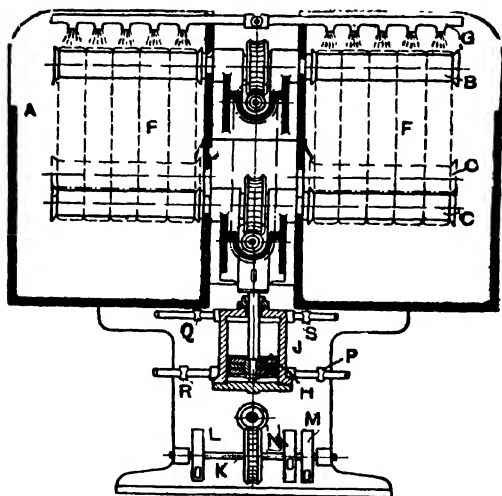
Fig. 85.
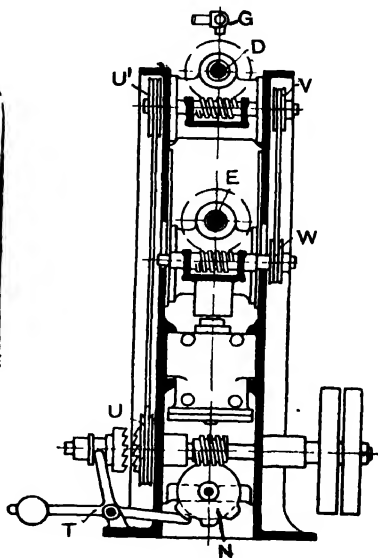
Fig. 86.

of augmenting the silkiness of the thread or of raising its lustre. This is illustrated in two sectional views in Figs. 85 and 86, and is composed of a closed vat or canal A in which are placed the two tiers of wooden, ebonite, etc., bobbins B and C, mounted on two shafts D and E. The hanks of silk F to be treated are stretched between these two sets of bobbins. Above each row of upper bobbins B is a distribution pipe G, through which the diluted acid or other liquid flows. The shafts of the bottom set of bobbins are fixed to the connecting-rod of a piston H which moves in its cylinder J. The piston is under the action of the distributors K, L, M and N, which

operate the valves P, Q, R and S, and the power may consist
of compressed air, water pressure, or other suitable agent.
By opening, for example, the valves P and Q, the compressed
air enters through P ; the piston rises and takes with it
shaft E, and the row of bobbins C are thus raised to a position
C^1. The hanks are naturally placed on and taken off the
bobbins when the bottom row occupies the high position.
Valve P is then closed and valve R opened. The piston H,
as well as the bobbins C, descend, and the hanks are thus
stretched in virtue of the weight of the piston and the bobbins
C. By an arrangement which couples the cam L to the
valve Q, and the disc M to the pressure valve S, this tension
can be augmented by a jet of compressed air directed against
the piston for a moment, such time being determined by the
speed of the shaft K and the discs L and M. When the cams
have made a revolution, the movements are repeated ; valve
S is closed, valve Q opened, piston H is raised, and the hanks
are stretched only by the weight of the bottom set of bobbins
C. At this moment the cam N, Fig. 86, presses down the
right end of lever T, and thus causes the vertical arm to slide
the teeth of the clutch into contact with the teeth on the
face of pulley U. Grooved pulleys U, U^1, V and W are
partially rotated, and they in turn communicate the motion
to the corresponding worm-shafts, and thence to the shafts
D and E. The hanks of silk are consequently moved inter-
mittently through a short distance so that all parts may
receive their share of the acid from the distributors G. It
will be seen that the object of the mechanism is to submit
the tensioned hanks to the action of the acid, and also for
an instant to relieve the tension during which the hanks are
moved forward to present a different part to the dropping
liquid. We will indicate in detail the most important of
Dr. Thiele's processes. He has applied to the solution of
cellulose in copper oxide the invention that Dr. Lehner made
several years ago, to draw out relatively thick threads of
nitro-cellulose. This process is now termed " stretch spinning."
We shall introduce a little later Dr. Lehner's process and
machine. Dr. Thiele also obtained a relatively thick thread
of cellulose in a very weak alkaline bath that only partially
precipitated the thread, and allowed it to be drawn out con-
siderably in the following manner : The thread, which
emerges from the capillary tube, is received into a funnel which

terminates in a bent pipe, relatively long. The other end of this pipe is fixed to a communicating vessel. In the funnel and in the bent tube is a very weak precipitating liquid, in which the thread is drawn out in virtue of its own weight, whereas in the communicating vessel, which is fixed to the other end of the pipe, the thread is received into a concentrated bath of soda or of potash, which precipitates the cellulose completely. The silk is then wound on to bobbins, or deposited into a receiver with a conical bottom so as to avoid any entanglement of the threads. In this way Thiele obtained a great number of very fine filaments of regular count, and comparable with the Despeissis artificial silk of Glanzstoff which has no more than twenty individual filaments. Thus Thiele's artificial silk approaches very nearly to natural silk in quality, touch, strength and use. This method of spinning artificial silk according to Lehner and Thiele's process has, in addition, another important technical value—it does away with the capillary orifices, and, consequently, with the obstructions that accompany them, and with the pressures.

Messrs. Fremery and Urban, directors of Glanzstoff Fabriken, lodged a patent in March, 1899, for drying artificial silk on large glass bobbins at a temperature of 40° C. (104° F.). These inventors discovered later that the long process of drying artificial textile products may be divided into two stages— a first and small part of the water evaporates very rapidly, whereas the remaining part is eliminated much more slowly. Fremery and Urban conclude from this fact that the second portion of water must be in chemical combination with the cellulose, and they have made experiments to diminish, if possible, this combination in order to obtain a more rapid drying process. In a supplementary patent the Glanzstoff Fabriken Company has indicated a practical result by making the bobbins pass through a warm bath of about 100° C. (212° F.) before drying, or submit the artificial silk for some minutes to a jet of steam. With either of these treatments it seems that the combination with water decreases to such a point that the time taken for drying the artificial silk is 60 to 70 per cent. less than that occupied by the older method. Dr. Ed. Thiele attacks this theory of the Glanzstoff Fabriken Company. He admits that the duration of the first drying is diminished by this process ; but this would be detrimental to the strength and elasticity of the threads, which in the

more or less pulpy state in which they exist at this time undergo a defective softening even in their constitution. Thiele thought of obtaining a more advantageous dehydration of the fibre by submitting the threads, dried for the first time, to an elevated temperature, and steeping them in boiling water, or subjecting them to superheated steam.

CHAPTER XIX

The Spinning of Artificial Silk on Continuous Machinery

WITHIN the last decade many attempts have been made to carry on simultaneously the operations of precipitation, spinning, copper removal, washing, twisting, drying, and reeling into hanks, and thus to produce by one and the same apparatus, or by a single machine, the finished artificial silk thread. There is obviously a considerable advantage in eliminating, so to speak, the manual labour, and so reducing very much the net cost of the finished product. It appears quite probable that the time will come when all these operations in the manufacture of artificial silk will be performed in two machines —one dealing with chemical operations and the other with mechanical processes. In virtue of the attention and thought that are being devoted to this phase of the question, we feel confident that in the near future the work will be performed by machines and processes which, by their simplicity, will enable us rapidly to transform this industry, and to conduct it safely into greater prominence. Some time ago Dr. Lehner constructed a little machine by means of which he was able to produce the finished silk directly from the solution. We shall give shortly a description of this machine, which has been suggested for use in the manufacture of Chardonnet artificial silk, but which has not received industrial application.

E. W. Friedrich, of Brussels, has described an arrangement in the German Patent No. 172,264, in which the threads are received on an endless apron or cloth instead of winding them on to bobbins. This travelling apron becomes charged with the precipitated liquid drawn forward by the threads ; this liquid may be extracted later by pressure rollers, while the silk from which the copper requires removing is wound on little bobbins placed on the cloth and rotated by friction.

We suppose that it is the Friedrich apparatus that has given the Glanzstoff Fabriken Company the idea of constructing a continuous machine with endless aprons or cloths in order to be able, in the same operation, to submit the threads to

different baths—*e.g.*, precipitating, copper removal, and washing baths—and afterwards to dry the threads on heated cylinders as has been already recommended by Dr. Pauly in his patent of 1897. According to a patent lodged in Germany, the continuous machine of Glanzstoff Fabriken is composed of a series of successive endless cloths that receive the threads from the spinning frame and conduct them to the drying drums. These cloths are not horizontal, but inclined, and the threads, which are carried up, are exposed to the copper removal bath and the corresponding washing bath, the liquids
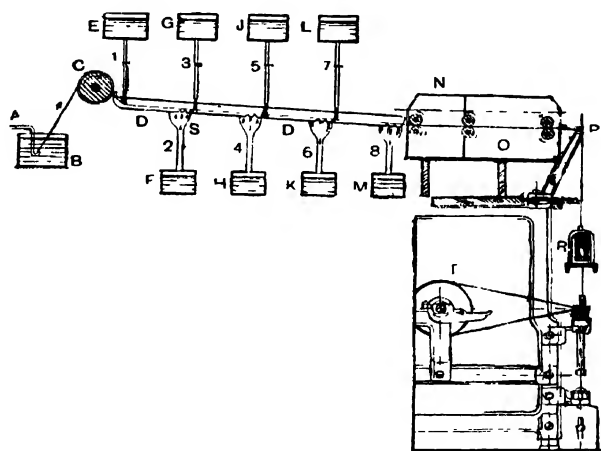
Fig. 87.

of which run in opposite directions. The fault of this arrangement is that these machines occupy a great amount of space, and are less accessible, seeing that it is necessary to have a special endless cloth for each liquid. It is also necessary to notice that the filaments of threads, which may break during the operation, are drawn in the opposite direction through these liquids. We do not know whether this process has been used successfully in the textile industry.

In the interval a German patent (No. 209,923) has been granted to J. Foltzer for a continuous method of spinning, the machine for which is illustrated in Fig. 87. The filaments issue from the multiple spinneret A into the coagulation bath, B, and then pass over guide roller C and into the canal or channel D. As the filaments pass down this channel they

come into contact with different liquids. A supplementary precipitating liquid flows from the tank E through pipe 1, and thus acts first on the threads ; this liquid flows out at S through pipe 2 into tank F. Similarly, in successive places in channel D other liquids flow simultaneously from tanks G, J and L, through pipes 3, 5 and 7, and flow out through pipes 4, 6 and 8 into tanks H, K and M.

Tank E contains the supplementary precipitating liquid ;
   ,,   G   ,,   the liquid for neutralizing the coagulating liquid ;
   ,,   J   ,,   the liquid for removing the copper ;
   ,,   L   ,,   the washing liquid.

The number of baths may, naturally, be reduced or increased according to requirements or to the process of manufacture. Three pairs of rollers convey the threads from the end of the channel D through a drying chamber O which is heated with hot air to the necessary temperature for drying the threads. The hot-air chamber O is closed at the top by hinged glazed covers N to facilitate the control. After the dried thread leaves the heated chamber O it passes through a thread guide P to the bobbin R, where it receives the desired amount of twist, and at the same time is wound on the bobbin. The bobbin R is mounted on a spindle, and the latter is driven in the usual way by a flat tape from the cylinder T. By this method the threads are precipitated, freed from copper, and washed by the various liquids that are introduced separately as shown, and which are prevented from coming into contact with each other. The different baths may be replenished and the liquid in each pair may be kept in continuous circulation— that is to say, the liquid in the tank F may be forced or drawn back into the tank E, and similarly with the other pairs of tanks. Since these machines are relatively long, one may always unite a series of four or five gutters to form a single channel in such a way that each part of the installation may be accessible to the workmen. When the last washing liquid L M is used at a high temperature, the silk dries more rapidly as it passes through the heated chamber O. The apparatus might be simplified still more by placing the spinneret A and the coagulating bath B close to the channel D, thus dispensing with the guide roller C. With such a provision no interruption would be offered to the thread between the spinneret and the drying chamber O, especially if an endless

cloth were passed round the three bottom rollers to conduct
the thread towards the thread guide P.

Another process that transforms the viscous mass into
artificial threads, and a process that differs absolutely from
all which have been described up to the present, consists in
forcing the solution between two grooved rollers, the grooves
corresponding to the thickness of the thread which it is
desired to make. Figs. 88 and 89 illustrate in elevation and
in plan the principle which is proposed by the inventor, Rudolf
Merves, of Berlin. The cellulose solution D is forced under
pressure into the compartment C through the inlet E, and by
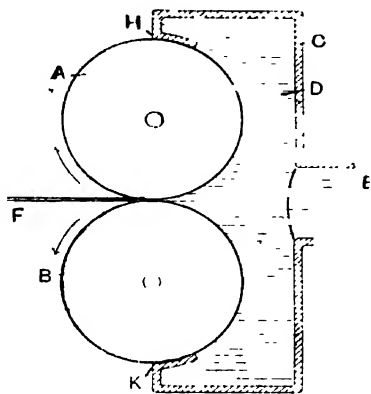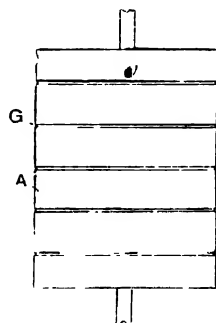
FIG. 88.   FIG. 89.

air pressure is forced between the two grooved rollers A and
B which clearly rotate in the direction indicated by the
arrows. The semi-circular grooves in the top cylinder coincide
and correspond exactly with the semi-circular grooves in the
bottom cylinder, the union of the two forming the size of
hole for the thread. Fig. 89 is a plan of part of the top
cylinder A, and shows five grooves G. According to the
inventor, it should be more easy to transform the viscous
mass into artificial threads by this method than through
capillary tubes or spinnerets, for the rotation of the rollers
A and B aids considerably in the disengagement of the threads.
To spin under pressure, the compartment C, which contains
the solution D, fits closely to the rollers A and B at H and K.
The threads F leave the rollers as shown, but a little farther
on they pass through another pair of rollers, not shown in the

figure ; the surface speed of the latter is a little greater than that of the rollers A and B, and the grooves slightly smaller, in consequence of which the threads are drawn out to a smaller diameter.   Another advantage is that the pressure which forces the solution through the grooves in the rollers may be considerably lower than that which is required for forcing the similar solution through capillary tubes.   We have not been able to ascertain if the industrial application of this principle has been successful ; at first sight it would appear very difficult to obtain by this method an artificial thread as fine, elastic and smooth as that which is obtained by the use of glass capillary tubes.

In a previous part of this work we have had occasion to speak about the method of counting the yarn.   The count of silk in hank is obtained in the well-known manner by means of a balance provided with a dial and pointer.   We have also mentioned the fact that for some time a machine has been employed which automatically registers the count. Lehner Fils' machine for registering the count, made and perfected by Messrs. Carl Hamel, of Chemnitz, Germany, does not require the same careful and conscientious girls as are required when the same work is done by hand, for the count is obtained independently of the attention or the inattention of the operative.   The girl has simply to suspend one hank after another, and always at the same place, and the machine does the rest rapidly, automatically and without errors.   Fig. 90 is a view of the complete machine, and Fig. 91 is a section.   A circle or concentric flat ring R rests on a table or fixed support on which it may rotate.   Fixed to this ring are 22 to 27 little balanced levers W of special construction, each of which is provided at its extremity with a little hook A, on which the girl places the hanks.   The other end, B, of the balanced lever W rests upon a support C.   A counter-balance weight G is capable of sliding on the lever W, and the whole function of the machine rests upon the sliding of this counterpoise G.   The girl, standing at point O, hangs the hank, the count of which is required, on to one of the hooks of the levers which pass in front of her as the ring rotates ; at this moment the balance weight G is near the extremity B of the lever W, and therefore farthest removed from point H, the fulcrum of the lever.   In this position, the force exerted by the balance weight being greater

than that due to the hank, the lever is held horizontally, and the extremity B rests upon the support C. By the rotation of the ring R, the hank-carrying levers W advance, and the
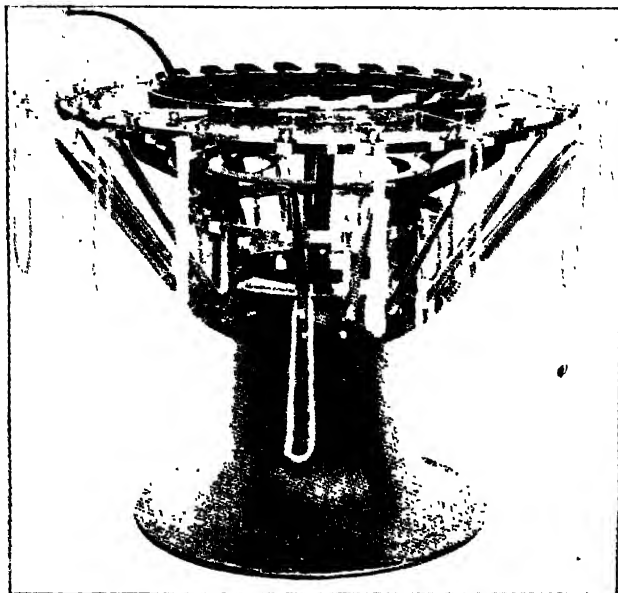
FIG. 90.
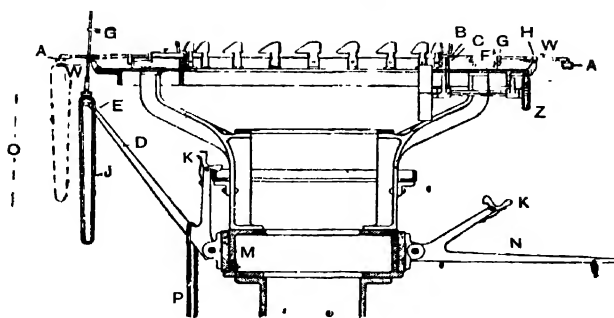
FIG. 91.

balance weights G come in contact successively with pieces F, having oblique surfaces and fixed to the table, the object of these being to cause the balance weights G to slide slowly

and gradually towards the fulcrum H of the lever W.   This gradual sliding movement continues until the balance weight and the hank are in equilibrium ; then any further movement of the weight towards H destroys the equilibrium, and the hank ultimately overbalances the lever W, which now assumes the position shown at J.   It is now a question of lifting off the hank, and this is done in the following manner.   Hinged to the periphery of the framework M under the table are 21 to 26 arms D, the pointed ends E of which occupy a position immediately under the hooks A upon which the hanks are suspended when the levers are in the vertical position J.   The counted hank is then taken by the pointed end E of arm D, is liberated from hook A, and then slides into the position P, whilst the disengaged hook continues its rotation.   The balanced levers all act in the same manner, are necessarily in equilibrium with equal weights at fixed places on the levers W, and hence each arm D can receive only hanks of the same count.   Before returning again to the place where the girl is stationed, the levers W, which are in the vertical position J, come into contact with and slide up inclined surfaces, while another part pushes the counter-balance weights G towards the point B, after which the whole system is ready to repeat the work.   The counted hanks are removed from time to time while the machine is working ; to effect the removal of the hanks, the arms D are placed in a horizontal position N by raising the catch K, which maintains them at other times in the position D.   The counting is naturally limited to a certain range of counts, but it is possible to increase the range by fixing a little supplementary balance weight to the extremity B of each lever W, and thus add a constant value to the force.   The machine is driven by a friction pulley Z which rotates the ring R, and with it all the parts of the apparatus.   Compared with the work done by hand, at the most 50 kgs. (110·2 lbs.) per day, the Lehner counter will pass 20,000 hanks of a mean count in ten hours—say, about 200 kgs. (440·8 lbs.) of artificial silk per day.

CHAPTER XX

Other Imitations of Natural Silk and the Apparatus for Producing Them

The spinning machine of the Count de Chardonnet is represented in end and front elevations in Figs. 92 and 93.

A is the pipe through which the solution passes to the machine.

C is a large cover which encloses A, and in which warm water circulates.

b is a socket which secures the capillary tube a to the fixed pipe in C, which pipe dips into the solution in A.

d is a little screw which serves to regulate the size of the opening by causing the pointed end to enter farther in or be withdrawn from the fixed pipe in C. The pointed end should be very close up to the pipe when a fine count is required, and be withdrawn proportionally for heavier counts.

G is a sleeve which encircles the capillary tube a, and cold water circulates between the sleeve and the tube. This cold water is stored in a tank situated in some elevated position, and flows through the pipe B, valve E, and pipe F; H is a gutter into which the water flows after having passed between the sleeve G and the capillary tube a.

O, O are threads of artificial silk which first pass singly through the thread guides M, made of copper rods, in groups of four as shown in Fig. 93, and then unite before passing through collector thread guides N, Fig. 92, to be wound on to the bobbin P.

L is one of a system of levers, which receives its movement from a part placed outside of the machine, not illustrated in the figures.

K are special nippers, joined to levers L. These nippers, which are illustrated in Fig. 94, piece or join up all broken threads which float on the surface of the water between sleeve G and the capillary tube a. The whole system of levers K, L is raised by the special mechanism in such a way that the ends m of the pincers K, in following the dotted line c, carry the broken threads up to the bobbin P, where they are caught and wound on. The pincers then return to the present position ready to repeat the operation automatically at proper intervals.

178
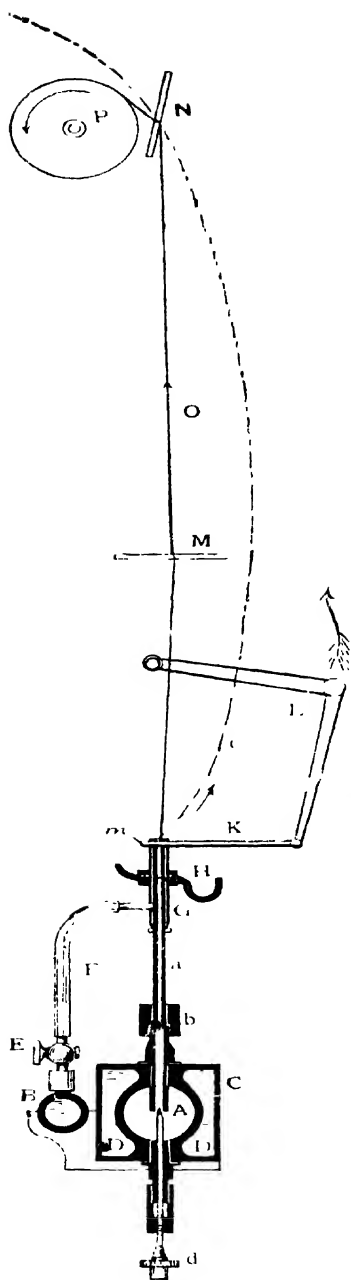
FIG. 92.
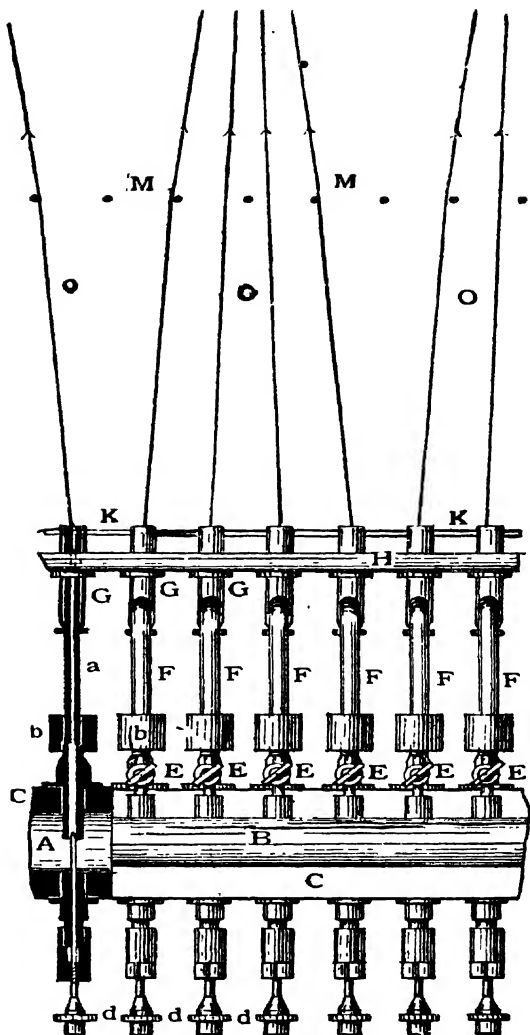
FIG. 93.
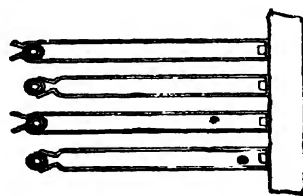
FIG. 94.

The aim of this system is clearly that of dispensing with piecers, but the Chardonnet works have again partially abandoned this arrangement.

The parts of Lehner's machine are illustrated in Fig. 95.

A is the valve through which the solution flows into the tank B, which is provided with a gauge glass Q. The level of the solution in tank B is practically constant.

C is a series of pipes which lead from the bottom of the tank B.
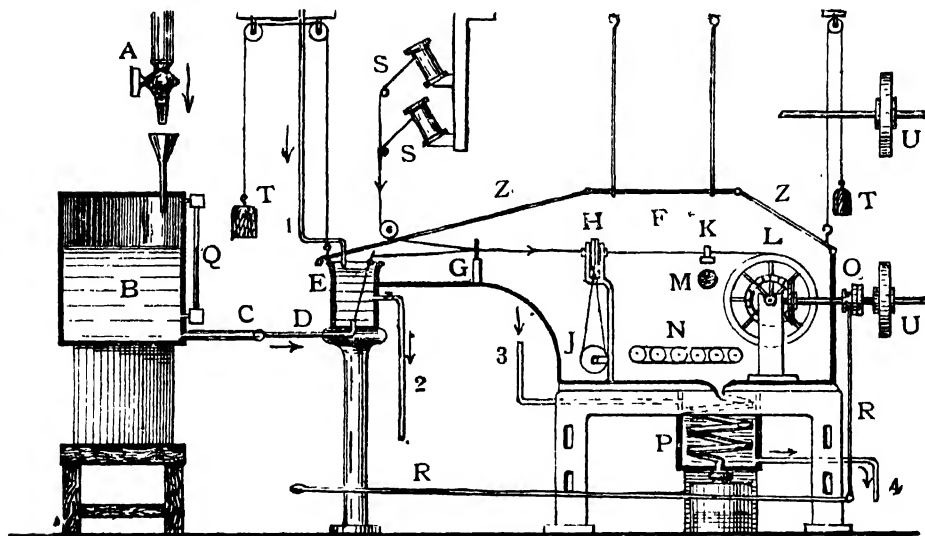
FIG. 95.

D are the capillary tubes, the bent ends of which project through the bottom of a narrow tank E filled with oil, turpentine, petrol, etc. This liquid is led into the tank E by pipe 1, and flows out through pipe 2; the valves of these two pipes must consequently be open in order that the level of the liquid in tank E may be always a little lower than the level of the solution in tank B, for it is this difference in pressure alone which forces the solution through the capillary tubes D. The thickness of the thread as it emerges from the capillary tube is too thick for most textile purposes, but it is drawn out to a smaller diameter as it passes at a given speed through the liquid in the tank E before being wound on the cylinder L. The ether, alcohol, etc., of the solution

B is in a great measure dissolved in the liquid in tank E, so that a strong thread of silk is obtained.

G is the collector thread guide.

H is an apparatus that receives its movement from a small pulley J and an endless band. The purpose of part H is to twist the artificial silk thread with one or more threads of natural silk, cotton, or wool, which come from the bobbins S, S and join the artificial silk thread at the collector thread guide G.

K is a thread guide with a lateral to-and-fro movement for cross-winding the twisted threads on the large cylinder L. Parts G, H, K and L are enclosed in space F, which is closed as completely as it is possible to be.

Z, Z are hinged lids balanced by the counterpoise weights T. These lids allow access to the interior F when it is necessary to piece the broken threads, to replace the filled cylinder, or for any other purpose.

N is a system of pipes through which cold water circulates to condense the vapours of ether, alcohol, etc. These condensed vapours pass through a serpentine or coiled pipe in the tank P cooled by a circulation of cold water which is led in by pipe 3 and flows out through pipe 4.

M is a heating pipe that partially dries the threads which are wound on cylinder L.

U, U is the motive power which drives the cylinders L.

R, R is a system of levers arranged instantaneously to stop any individual cylinder L.

Another apparatus by Dr. Lehner for transforming solutions into artificial silk is illustrated in Fig. 96. The solution coming from the tank A flows through the pipe B, and out of the spinneret C on to the surface of a cylinder D which rotates at a uniform speed on the axis E and in the direction indicated by the arrow. In order to solidify the threads that are formed at C, a segment of the cylinder D is provided with a double envelope F kept at an elevated temperature by the heating pipe G. In consequence of the heat, the moisture in the threads is evaporated quickly, and the thread solidifies. The rotation of the cylinder D causes the evaporated liquids to run into the concavity H, where the vapours liquefy in consequence of the lower temperature, and flow into the vessel I. The perforated iron plates V, fixed in the concavity H, are for the purpose of keeping the vapours as long as

possible in contact with the surface of the cooling envelope
S. The heated envelope of evaporator F is insulated from the
surface of the cooler S by insulating material W, which also
insulates the upper part U of the envelope. The artificial
silk threads N, partially or perfectly dried, emerge at L,
whilst a rotating brush T lifts broken filaments from the sur-
face—filaments that would otherwise collect on the surface of
the cylinder. A pad Z, faced with felt, absorbs the moisture.

Dr. Lehner also indicates that cotton, silk, or other threads
may join the artificial threads at C and thus obtain a com-

pound thread more or less
agglutinated, and one
that may be delivered
in a similar manner at L.
Instead of spinning arti-
ficial silk, one might even
impregnate natural fila-
ments with cellulose solu-
tions, and dry them in a
similar way on a rotating
cylinder. Dr. Lehner had
proposed this installation
for the spinning of nitro-
cellulose and other solu-
tions, whilst the Glanzstoff
Fabriken Company, much
later, applied in the
cuprammonium process
the process of drying on
rotating drums at a high
temperature.
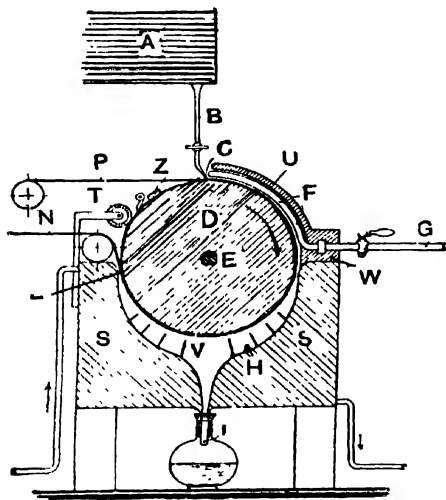
Fig. 96.

Amongst the numerous inventions of Dr. Lehner, of Zurich,
may be mentioned his spinning apparatus illustrated in Fig.
97. The solution is in tank A, and passes through the pipe
B and the spinneret E into a glass cylinder D, where it is
transformed into threads. The spinneret E is joined to pipe
B by a piece of indiarubber tubing C. The glass cylinder D
contains the coagulating liquid which flows as required through
the pipe F, absorbs the solvent of the cellulose while coag-
ulating the cellulose, and then flows through the small pipe
I into another glass vessel L of the same height as D. Neither
vessel D nor vessel L is airtight, but both are simply covered
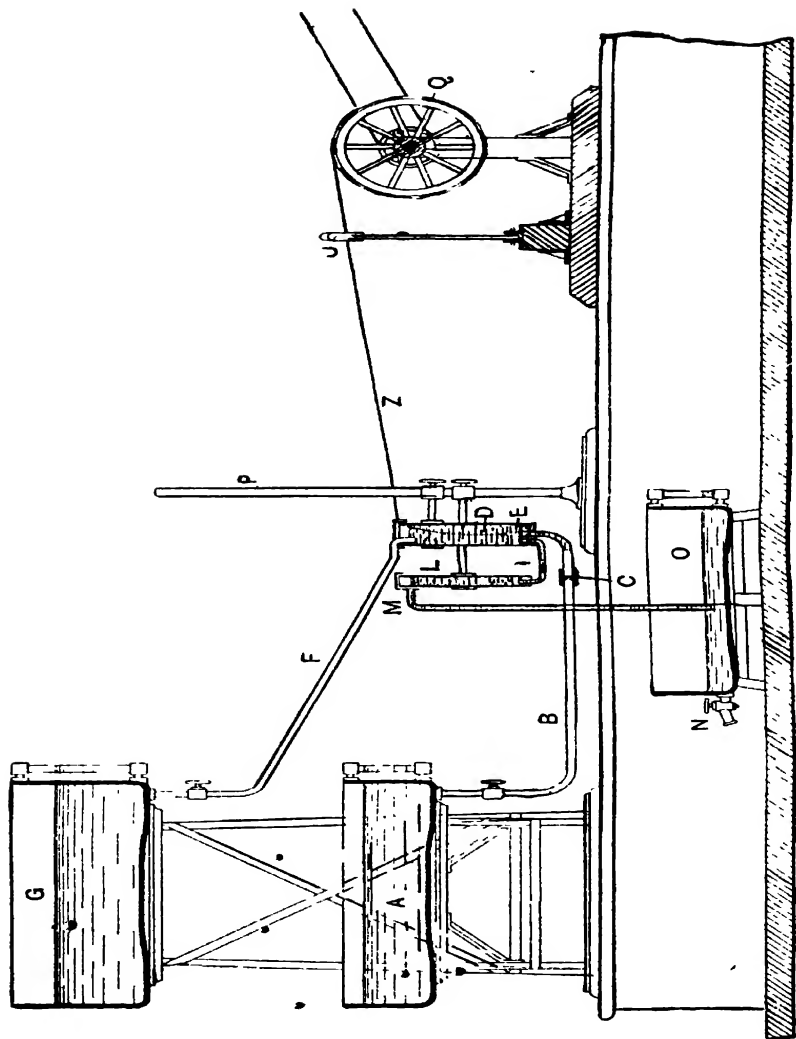
FIG. 97.

with lids. The mixture of the two liquids—*i.e.*, of the coagulating liquid and of the solvent of the cellulose—flows through the pipe M into the tank O, which is arranged so that it may be emptied by means of the valve N. The thread Z passes through a thread guide U, and is wound on to the cylinder Q. The silk is formed as follows : The filament emerges from the capillary tube E relatively thick, and is drawn out or stretched in the bath of cylinder D as it is being coagulated. The degree of fineness to which the thread is drawn depends upon the speed of the cylinder Q—the higher the speed the finer will the thread be drawn.

Bernard Loewe, of Paris, drops the threads from the spinning frame into an open box, where they are arranged in regular spiral form, and dried without tension. When a box is full and contains sufficient to form a hank, it is replaced by another one. This arrangement is employed for the nitro-cellulose process. On account of being "dried without tension, the silk is less lustrous than those artificial silk threads which are dried under tension.

For the manufacture of viscose, C. Leclaire, of Paris, has mentioned a process by which he prepares the viscous mass in a tank ; the tank may be hermetically sealed, and may be rotated in order to effect the mixture. The different chemical agents, some in a liquid state, others in a gaseous state, are introduced successively under pressure, whilst the gases of vapours formed are withdrawn by aspiration. The apparatus is provided with a double casing through which warm liquids or refrigerants may circulate, so that the temperature of the mass in formation may be varied according to requirements. The interior of the apparatus is electrically lighted, which enables the process to be followed.

La Fabrique de Soie Artificielle de Tubize, near Brussels (French Patent No. 412,887), encloses its spinning machines almost hermetically by partitions of wood and glass, and sucks in alcoholic and etheric vapours through the bottom, whilst the sliding windows render the whole of the top part of the machine accessible to the workers. The alcoholic and etheric vapours may be recovered in this process.

A similar process of recovery is described in the French Patent No. 416,064, by J. Fournaud, whereas De Chardonnet (French Patent No. 413,359) recovers the alcohol and the ether which still remains in the threads on the bobbins as they

leave the spinning frames, by placing the bobbins before winding into water.   He surrounds these bobbins impregnated with water with a very light cylinder—say, an aluminium one. The bobbins are mounted on a spindle, and by rotating them rapidly, the water, which contains alcohol and ether, is extracted by centrifugal force, and flows into another cylinder on small receiving vessel.   In order to reduce the length of the spinning machine, and thus concentrate the vapours of alcohol and ether, De Chardonnet mounts the spinnerets (which up to this time were arranged on long distributors) in the form of a circular flat plate which may be rotated.

La Soie Artificielle de Vivier, also called " Soie de France " (*French Silk*).—This produce is obtained by dissolving pyroxyl (tri-nitro-cellulose) and gelatine in glacial acetic acid.   The coagulation of this product is effected as the solution emerges from the orifice of the capillary tube, and results in a thread which must pass through three baths of different composition before its formation is complete.   Afterwards the thread passes to the crystallizing vessel, where it is dried at a low temperature ;   it is then taken to the reeling department, where it is made up into hanks and allowed to remain in water.

There is also the *Cadoret* process, by means of which a kind of artificial silk is manufactured from old cotton rags cleaned with caustic soda.   The original cost of manufacturing this silk was only about 6 frs. 50 c. per kilogramme (2s. 4·1d. per lb.).   Cadoret does not use a liquid solution, but a plastic composition which is transformed into threads.

Serret Silk.—We have seen some very beautiful samples of Serret silk, and this product has a characteristic appearance. The inventor produces this substance by dissolving the waste of natural silk in an acid or an alkali under determined conditions, without which the substance would be altered in solution.   For the same purpose he neutralizes immediately the resulting solution by adding water to it, or, better still, by lowering the temperature.   The transformation into threads is effected according to the ordinary methods.

Dr. Carl Hofmann, of Munich, manufactures threads and other artificial textile products in the following manner.   He makes a mixture, say, for example, of 300 cubic centimetres (0·066 gal.) of concentrated phosphoric acid and 300 cubic centimetres of acetic acid, and to this he adds 20 to 25 grms. (308 to 385 grains) of cellulose.   The whole is then mixed until

a viscous substance is obtained, and this substance is then forced through the openings of capillary tubes into a coagulating liquid, which may be water or alcohol. Dr. Hofmann hopes to be able to make more solid and lustrous products when, after coagulation, he washes and dries the threads under tension.

La Société Anonyme Le Crinoid of Rouen, where the cuprammonium process is employed, has patented the following process : In coagulating the threads in an alkaline bath, it happens, after a certain time, that, in consequence of the copper and ammonia which are retained in the bath, the liquid becomes so dark that it is a difficult matter for the piecers to distinguish and to recover the broken threads. Other industrial establishments have already encountered this difficulty, which they try to avoid by adding glucose and saccharose to the precipitating liquid with the object of reducing, at a raised temperature, the copper salts to metallic copper or to cuprous oxide. In order to operate at temperatures as little above the normal as possible, and in an economical manner, the Crinoid Company effect this reduction by the addition of a solution of formaldehyde. To perform the work to advantage, the proportion should be about 1·5 per cent. of 40 per cent. formaldehyde solution to the precipitating liquid. This quantity is sufficient to reduce the copper salts in solution in a precipitating bath composed of caustic soda and carbonate of soda at a temperature of 40° C. (104° F.). A surplus of 5 per cent. of formaldehyde solution improves, on the other hand, the coagulation of the threads, which become, by this means, stronger and less sensible to moisture ; this has been known for some time.

An interesting process, and one which has for its object that of obtaining more solid, elastic and washable threads, has been proposed by Theodor Eck, of Lodz. He precipitates the artificial silk in soda or potash of 30° to 40° Bé., and containing about 10 parts of soda, $1\frac{1}{2}$ to 2 parts of methyl-alcohol of 99 per cent. An analogous process had been previously indicated in the ' French Patent No. 369,957. After removing the copper, and washing the threads, Theodor Eck introduces them again into caustic lye at 20° to 40° Bé. containing a fixed quantity of common salt.

The same inventor, Theodor Eck, has also endeavoured to prevent the decomposition of the cellulose solution when it

is not kept at a low temperature, by making a mixture of ammoniacal copper (cupric) oxide and ammoniacal cuprous oxide. The presence of the cuprous oxide in the solution prevents all oxidation of the cellulose, and such a solution, says Theodor Eck, may be kept at the ordinary temperature without undergoing any change. The industrial value of this process, like all others, can be judged only after it has been confirmed by practice in works where artificial silk is regularly made on a large scale. Small quantities of artificial silk are made by all sorts of processes, and the silk thus made possesses, according to the inventors, considerable advantages of some kind or other, and capable of yielding superior yarns ; but the yarn, when ultimately made, is often classed only as third or fourth quality, and is parted with at almost any price in order to get rid of it. The solutions of cuprous oxide, of which we have just spoken, contain the same percentage of cellulose, and are thicker than the simple solutions of copper oxide. A solution of cuprous oxide, containing, for example, 3 per cent. of cellulose, corresponds in viscosity with a 4 per cent. of cellulose which does not contain cuprous oxide. By this process one has the advantage of being able to employ larger capillary tubes ; therefore, with the same opening in the capillary tubes, and the same percentage of cotton, it is possible to obtain by the use of cuprous oxide finer threads than can be obtained without its use.

J. Foltzer employs a mixture of copper oxide and ammoniacal copper sulphate to obtain more constant solutions. The proportions maintained are the following : To 50 parts of copper oxide (specific gravity 1·000 to 1·004) prepared in the ordinary manner, is added a solution of copper sulphate containing about 27 grms. to one litre of water (415·8 grains to 0·22 gal.) ; these substances are intimately united in a mixing tank for some minutes, and then 10 parts of a 15 per cent. solution of caustic soda are added. The combined materials are further mixed for five minutes, and to 800 litres (176 gals.) of this liquid are added about 107 kgs. (235·8 lbs.) of dry cotton, which is perfectly dissolved in twelve to fifteen hours.

Recently, the Foltzer processes have been considerably improved for the manufacture of artificial silk and hair. The manufacture of artificial leather and fabrics is also conducted successfully in Mr. Foltzer's factory in Riedikon-Uster,

Switzerland. Similar goods are also made by M.M. Lefebrre-Horent Frères, at Loos-lez-Lille, France ; at the works of Figli di Luigi Zignone at Quarona-Sesia, Italy ; and by the Soc. Ame. Edouard Keffel at Kohlmühle, Germany.

Henry Bernstein, of Philadelphia, technician to the American Artificial Fibre Company, prepares a solution of ammoniacal copper oxide, in which he mixes sugar and molasses to prevent decomposition when the temperature is raised. His process is as follows : 2 per cent. of sugar or molasses is mixed with 20 per cent. of ammonia ; small pieces of copper are then introduced, and by means of a current of air the oxidation is effected. A proportion of 8 per cent. of cellulose is dissolved in the prepared copper oxide, and the solution may be kept at the ordinary temperature without decomposition.

The Rheinische Kunstseide Fabrik at Goch, Germany, mixes copper sulphate, ammonia and caustic potash for the solutions of cellulose. In principle this process is the same as that of the French inventor Prud'homme, which we have already described in all its details. The Rheinische Kunstseide Fabrik, however, makes the interesting observation that the solutions composed of copper salts cannot be kept without deposition of copper and cellulose, and these being carried forward render the satisfactory production of artificial silk by industrial processes nearly impossible ; the threads break frequently at the spinning frame, and the openings of the spinnerets or capillary tubes are very often either partially or wholly obstructed. Owing to this fact the prepared threads are not only irregular, but they also lack the lustre and suppleness which are characteristic features of perfectly made threads ; many artificial silk manufacturers have encountered the difficulties of this process without being able to overcome them. The Rheinische Kunstseide Fabrik says that it is possible to avoid this defect by cooling the copper sulphate solution before adding the cellulose to be dissolved. This cooling process results in a deposition of copper salts which may be separated by filtering. The filtered solution dissolves perfectly the same amount of cellulose as before, and the substance keeps well at the ordinary temperature without forming a new deposit.

Another process of the Rheinische Kunstseide Fabrik consists in preparing the liquid for dissolving the cellulose with copper sulphate, ammonia and caustic soda, and, before

dissolving the cotton in it, adding to the mixture tartaric acid or oxalic acid. The addition of these organic acids makes a more constant solution, and according to the Rheinische Kunstseide Fabrik it is possible by this process to prepare the solution for several months in advance without any fear of decomposition. The inventors also claim that the solution of cellulose is much more rapid and more complete when organic acids are added to the solvent. The following particulars indicate the process : One to three parts of copper sulphate are mixed with two to four parts of a caustic soda solution of 21° Bé , and five to fifteen parts of ammonia at 25° Bé. To this mixture is added about 0·1 part of tartaric acid. With the same object of making the solution more stable, the Glanzfäden Aktiengesellschaft, of Berlin, before or after dissolving the cotton, add hydrocarbons in the proportion of 25 per cent. of the weight of the dissolved cellulose. The same and many other inventors have described similar series of processes, the values of which have yet to be confirmed in practice—processes that would take up too much space in this work, and therefore cannot be dwelt on. None of these processes, however, gives such good results, financial and otherwise, as the simple reagent of Schweitzer, or the process with ammoniacal copper oxide as invented by Despeissis.

Ph. Bechtel made an effort to reduce the net cost of artificial silk by making a mixture of cellulose solution and undissolved particles of fibres, which he pounded mechanically, as is done, for example, in paper works. He selected the particular fibres by using a sieve which allowed fibres of only 0·3 to 0·5 mm. in length to pass through. He hoped to be able to mix about 50 per cent. of the fibres to the solution, and to obtain a good silk by spinning this mixture through capillary tubes with openings of about 0·5 mm. diameter. We have not heard, however, whether this process has been conducted on an industrial basis.

La Compagnie française des Applications de la Cellulose (copper-oxide process) has described the following method of preparing a concentrated solution of cellulose : 30 kgs. (66·12 lbs.) of cotton freed from grease and slightly bleached are pulverized and afterwards diluted with 300 to 600 litres (66 to 132 gals.) of water. Then 60 kgs. (132·24 lbs.) of copper sulphate are dissolved in 300 to 400 litres (66 to 88 gals.) of

water and added to 40 litres (8·8 gals.) of caustic soda diluted
with three or four times its volume of water, and kept at the
ordinary temperature whilst being kept in motion in a mixing
tank. If proper precautions are taken there need not be
any rise of temperature. It may be an advantage to add a
small quantity of sugar to the caustic soda. Afterwards the
two solutions are mixed, and the liquid, prepared with the
pulverized cellulose, absorbs immediately the copper hydroxide.
The cellulose is afterwards separated in a hydro-extractor or
in a filter. The product thus treated has a beautiful blue
colour, which it retains a long time. To prepare afterwards
the solution of cellulose for the spinning process, the hydroxide
of copper is mixed with about 100 litres (22 gals.) of ammonia
at 28° Bé. The mixing is continued for fifteen to twenty
minutes, after which the substance is allowed to remain for
about 24 hours, when the solution is complete. It is a good
plan to run the mixer for a few minutes from time to time
during this otherwise period of rest. The solution may be
hastened by adding, during the operation, small quantities
of caustic soda at 38° Bé. diluted with an equal volume of
water. This addition of caustic soda prevents the final
solution from being too thick, and also facilitates the filtration.
By this method it is possible to dissolve as much as 15 per
cent. of cellulose, and at the same time to obtain perfectly
homogeneous solutions.

Rudolf Pawlikowski, of Goerlitz, describes in the German
Patent No. 237,200 a process that may be of practical
interest. The inventor states that it is known how to wind
wet threads from the spinning bobbin and to twist them.
By this process the copper is removed, and the operations
of washing and drying performed with the thread on the
reel. This method of passing the thread through successive
baths entails much time, demands a considerable installation,
and involves a large amount of hand labour in the transference
of the reels from one bath to the other. The inventor seeks
to avoid these defects as follows : The copper is removed
from the silk, and the latter is washed before it leaves the
spinning bobbin ; twist is afterwards imparted to the thread
by rotating the bobbin on a spindle, and at the same time
the thread is wound on a heated cylinder and dried. The
artificial silk is therefore finished and twisted in a single opera-
tion. This process resembles closely that of Donnersmarck,

in which the silk is dried on the spinning bobbin before being reeled and twisted.

Pawlikowski's method also resembles very much that of the Glanzstoff Fabriken Company. It differs from it, however, in that whereas Pawlikowski twists the threads in a wet state, the Glanzstoff Fabriken Company first dries the threads on a heated drum and imparts the twist afterwards. All these processes appear to yield practical results with small quantities. We have also attempted to twist the threads from the copper-oxide process before removing the copper both in the wet and dry states, and also when the copper has been removed and the threads still charged with water, and we must admit that practically it is a very difficult matter to operate successfully in any of the cases. The silk that has been dried without removing the copper is too weak to undergo all the subsequent processes—the twisting especially fatigues considerably the threads in formation.

Another process (American patent, Foltzer), and one which gives sufficiently good practical results, consists in reeling the blue artificial silk threads which still contain copper, ammonia and a sufficient quantity of caustic soda or caustic potash from the precipitating baths to render them sticky, and thus facilitate the winding. The copper is removed from the threads, which are then washed and ultimately bleached, or even dyed, on special reels, and the latter, in order to avoid all handling, are placed in a porcelain or glass vessel in which flow successively and alternately the different liquids for removing copper, for washing, etc. The twisting is performed last of all when winding the silk from hanks on to bobbins for the weaving department. There are machines in the textile industry which impart twist to the threads as the latter are being wound from hank to bobbin—machines which may be found practicable for the artificial silk industry.

The British Patent No. 19,107 (1906) and the German Patent No. 240,751 (1908) of Dr. L. Lederer describe processes by which it is hoped to solve the problem of washable and inflammable artificial silk and pellicles ; the former proposes to employ acetylated nitro-cellulose, and the latter a mixture of nitro-cellulose and acetate of cellulose. Much has been said about the processes of acetylated cellulose of Lederer and other chemists, and the opinion has often been expressed that the artificial silk made from such substances was destined

to supplant in a short time other artificial silks, as well as natural silk. Most of these acetates have remained, up to a short time ago, in the experimental stages of a non-inflammable pellicle, and a pretended washable artificial silk. But so far the celluloid pellicle is stronger, cheaper, and perhaps more supple, than that made from acetate. The original attempts to manufacture artificial silk from acetate were unsuccessful, but they are now well made by a few firms (see " Celanese," Chap. XV) ; it was not so much the net price of the silk as the quality which was the cause of its original failure. There are two methods of manufacture connected with the spinning of acetate of cellulose—dry spinning as in the case of Chardonnet silk, and wet spinning—as, for example, the process of Depeissis and Lehner. In wet spinning the thread passes into a precipitating bath, whereas in dry spinning the thread is formed before it leaves the capillary tube, and a precipitation bath is not required. In most cases dry spinning has been abandoned, the attempts to spin from acetate being practically confined to the wet process. The part played by the liquid in which the spinning is conducted is that of absorbing the volatile solvent of the solution while providing the necessary heat for volatilization. For example, a solution of calcium chloride is qualified to play this part, since it absorbs the solvent of the acetate and coagulates the latter in the form of a thread which may be wound on to a bobbin. In place of calcium chloride, any other substance may be used which absorbs, with evolution of heat, the acetone or alcohol employed for dissolving the acetate—as, for example, dilute sulphuric acid or zinc chloride. One to two atmospheres pressure are sufficient for the purpose of spinning solutions of acetate made, for example, of 40 volumes of acetone and 10 volumes of alcohol of about 95°. The coagulating solution should be concentrated, say, 50 grms. (770 grains) of $CaCl_2$ to 100 cc. (0.022gal.) of water.

Delpech has published in the review " Le caoutchouc et la gutta percha " of 15th June, 1911, the result of some experiments on acetate spinning, in which he states : " According to the diameter of the capillary tubes employed, the silk obtained is more or less supple. Ii the diameter of the filaments is arranged to be from ·05 to ·06 mm., the acetate silk is strong, supple and silky ; its appearance approaches that of good natural silk ; it is not so lustrous as the artificial silk made by either the Chardonnet process or the cuprammonium

process—this is not a defect, however, but rather an advantage. Its great disadvantage is its weakness, for, according to Delpech, it is much weaker than Chardonnet silk, and, moreover, when wet it loses one-third of its strength.[1]

Dr. A. Eichengrün, of Berlin, has also studied greatly acetylated cellulose, as evidenced by his French Patent No. 412,797, and also the addition to the French Patent of No. 12,388. We might also mention the French Patent No. 418,309 of Farbenfabriken Friedr. Bayer & Co., of Elberfeld ; but as these inventors employ their solutions specially for the manufacture of varnishes and pellicles, it is unnecessary to dwell upon them here.

Professor Dr. A. Herzog, of Sorau, who has made microscopic researches on acetate silk, has found the mean thickness of threads to be $42 \cdot 3 \mu$, where $\mu = 0 \cdot 001$ mm., that the regularity of the filaments is greater than that of other artificial silks, and that the flatness of the thread is very rare. The section of the fibre is oval or round. Unlike other artificial silks, acetate silk scarcely swells under the influence of water.

According to Hassak and Herzog, the strength of acetate silk compared with other artificial silks and natural silk is as follows—

Type of Silk.	Dry State.	Wet State.
Natural silk	37·0	37·0
Chardonnet silk	12·0	2·2
Lehner silk	16·9	1·5
Cuprammonium silk	19·1	3·2
Acetate silk	10·2	5·8

According to these observations, there is a considerable loss of strength in the wet state ; but of all the artificial silks, that of acetate is the strongest in the wet state.

The Glanzstoff Fabriken, of Elberfeld (British Patent No. 15,700, 1910 ; and the Patent No. 6241, 1911) state that cellulose hydrates, which can be obtained in large quantities at a low price in the form of denitrated nitro-cellulose threads, lustro-cellulose threads (cuprammonium process), viscose threads, and waste from the cellulose artificial silk industry, are highly adapted for use as the raw material for the manufacture of formyl-celluloses. It is only necessary to introduce the above materials into ordinary formic acid of about 95 per

[1] This defect has now been eliminated, see p. 100.—*Transr.*

cent. to 100 per cent. strength, and to warm gently up to 40° to 50° C. (104° to 122° F.), when an inexpensive solution of formyl-cellulose is obtained which can be employed directly for the formation of artificial silk threads, pellicles, etc. High temperatures have a more rapid action on the cellulose, but in this case the solutions are too thin instead of being sufficiently viscous, and the elastic and lustrous pellicles and threads are no longer obtained. The proportion of cellulose dissolved must not exceed 6 per cent. Any kind of artificial silk waste may be used, when this waste has been previously coagulated, the copper removed, and the substance washed and dried. The cellulose may be dyed before formylation with colours resistant to acids, in which case it is unnecessary to dye the finished products. Several inventors have spoken in praise of the method of dyeing cellulose before it is dissolved ; nevertheless, and in spite of the good results that have been obtained, we have, after having performed industrial trials ourselves, come to the conclusion that this method of working is not practicable, seeing that it is necessary to clean very carefully all the apparatus when a change is made from one colour to another. This cleaning process, which may be easily performed in a laboratory, is not such a simple matter in an industrial establishment ; the hand labour and the waste which result, for example, in the cleaning of the mixing tanks, the system of pipes, etc., would more than counterbalance the advantages that would attend the previous dyeing of the cellulose.

According to another process of the Glanzstoff Fabriken Company, ten parts of artificial silk waste (cellulose) may be dissolved in 100 parts of formic acid, to which are added about fifty parts of lactic acid. The excess of formic acid is removed by creating a vacuum while the solution is at a low temperature, say, about 40° C. (104° F.). The formic acid is thus evaporated, and perhaps may be recovered in another operation. The viscous mass which remains is transformed into artificial silk or pellicles. Already, in 1901, a similar process was described by Waite in the American Patent No. 690,211.

The Donnersmarck'sche Zelluloseester-Gesellschaft in Germany have described a process in which lactic acid is replaced by phosphoric acid. The best proportions appear to be a mixture of 1 kg. (2·204 lbs.) of formic acid of about 99 per cent with 1 kg. of phosphoric acid, 84 per cent., to which is

added 200 grms. (about 7 ozs.) of cotton—cleaned and slightly bleached cellulose. The solution is accomplished in a few hours.

The German Patent No. 250,281, from the firm of S. Diesser, of Zurich, Switzerland, indicates a process by which they render elastic artificial products made from a solution of albumen and formic acid. As mentioned by S. Diesser, it is already known that albumen dissolves in cold formic acid. If from this solution the acid is evaporated, there remains a residue which can be redissolved in water, but which is hard and brittle after being dried. Attempts have been made to make these textile products and pellicles supple and elastic by the addition of different substances. With this end in view the inventor has found that the products of condensation obtained by the action of formaldehyde on phenol were capable of yielding elasticity. Indeed, if a solution of albumen and formic acid be evaporated and spread on a glass plate, a supple, elastic and transparent pellicle, proof against water, will be obtained, provided that care has been taken to stir the above products of condensation during the evaporation. For example, to 20 grms. (308 grains) of a 10 per cent. solution of albumen in formic acid of 1·22 specific gravity are added ten drops of a cold saturated solution of oxalic acid in formic acid of specific gravity 1·22. The formic acid is evaporated, and the resulting pellicle is left for three minutes in a bath of formalin (formic aldehyde) at the ordinary temperature. It is then heated for three minutes, rinsed several times in water, and dried.

The Langhans process consists in transforming the cellulose into a plastic material of perfect homogeneity by submitting it for a very short time to a sulphuric acid bath sufficiently weak to prevent gelatinization. When working at a temperature of 15° C. (59° F.) it is necessary to employ sulphuric acid at 40 to 50 per cent. Immediately afterwards the substance is exposed to the action of sulphuric acid, sufficiently concentrated, say, 70 to 80 per cent., to effect the solution of the cellulose, with the formation of sulpho-cellulose. This concentrated acid is added little by little, stirring all the time, until a consistent gelatin is obtained. In order to prevent the gelatin from decomposing during the time which elapses before transferring it into threads, it is necessary to dilute the concentrated acid by adding to it, during the mixing, a weak sulphuric acid of about 45 to 63 per cent.

Langhans states that water may be used for diluting, but that it produces immediately an augmentation of temperature which is injurious to the solution because it liquefies very rapidly instead of remaining viscous. In his French treatise on artificial silk, published in 1903, J. Foltzer describes experiments which he made, and states that it is possible to obtain constant solutions, even when diluting with water, when the work is conducted in the cold. In fact, if the cellulose be dissolved in sulphuric acid at a low temperature, and the solution be kept, say, at 0° C. (32° F.), or even at a rather lower temperature, excellent results follow, and the artificial silk thus obtained is elastic and lustrous ; it presents at the same time a parchment-like character, is tolerably indifferent to the action of water, and has the same characteristic features as other products of artificial silk, such as artificial hair, pellicles and threads, which may be manufactured from these solutions. One might expect that the prevalence of low temperatures would have a good influence on cellulose during solution in sulphuric acid, as happens for many other cellulose solutions. We may say, however, that the artificial threads obtained by this process are neither as white nor as strong as those made from viscose and the ammoniacal copper oxide process with precipitation by alkalis. Nevertheless, seeing that the price of this solution does not reach more than 1·30 francs per kilogramme (5·67d. per lb.) of dissolved cellulose, one might reasonably expect to see some day or other the establishment of this process by sulphuric acid raised to a practical and industrial standard.

Dr. E. Berl, of Brussels, who has returned to the study of this process, German Patent No. 259,248, April, 1912, has also recognized the advantageous effects on the solution of cellulose in sulphuric acid when low temperatures prevail. He dissolved one part of dried, cooled and opened cotton in twelve parts of sulphuric acid at 60 to 77 per cent., and at a temperature of − 15° C. (5° F.). Dr. Berl claims in his patent these very low temperatures, and says that to obtain masses more viscous it is necessary to operate. say, at − 5° C. (23° F.). After the mixing he allows the solutions to remain for some time, then filters them, drives off the air bubbles, and transforms the solution into artificial threads or pellicles. A new departure in Berl's patent is the employment, for regulation purposes, of an alcohol of 50 per cent.—say, for example,

ethyl alcohol or methyl alcohol, and cooled to a temperature of $-20°$ C. ($-4°$ F.). Further, the inventor states that if the employment of a low temperature be extended to the coagulation baths, more elastic products are obtained. As already remarked by Langhans, weak acids may also be employed for precipitating cellulose when care is taken to keep the precipitating liquid cold--according to Dr. Berl, at a minimum temperature of $-10°$ C. ($14°$ F.).

Dr. C. G. Schwalbe, of Darmstadt, Germany, refers to the treatment of vegetable fibres with sulphite for obtaining cellulose, a treatment which consists in adding to the solution of the neutral sulphite an acid in aqueous solution, or in the shape of a gas, or of an acid salt, or in gradually introducing the substance during the boiling process ; the quantity of acid thus employed before the end of the treatment is not more than that corresponding to half the equivalent of the quantity of sulphite used.

F. Seaton, Snowdon, and D. A. Young, London, refer to the manufacture of cellulose acetate or acetyl-cellulose to render the product non-inflammable. The washing is divided into two or more stages, the first taking place after the acetylization of the cellulose is completed. The second and any further washings are performed in a sufficient quantity of water to which has been added boracic acid or a suitable borate, equivalent in weight to about $2\frac{1}{2}$ per cent. of the cellulose acetate to be treated, and in this solution the cellulose acetate is well agitated to render it flameproof.

The process of the Vereinigte Kunstseide-Fabriken, of Frankfort-on-Main : According to this process the hydrated cellulose is dissolved in a weak solution of caustic soda or caustic potash of 3 to 4 per cent., and precipitated in an acid in the form of threads or pellicles.

First Example : 100 parts of artificial silk thread waste are dissolved in 100 parts of a solution of caustic soda of 1·120 specific gravity, and are re-precipitated and transformed into threads in an acid of mean concentration.

Second Example : 10 parts of cotton cellulose are mixed rapidly with 100 parts of sulphuric acid of $60°$ Bé. As soon as the mixture is uniform it is removed in small portions into a sufficient quantity of water. The hydrated cellulose thus obtained is well washed, squeezed to remove the water, and dissolved in 100 parts of a solution of caustic soda of specific

gravity 1·120. With the aim of increasing the lustre, the adhesion and the strength of the threads, the hydrated cellulose may be dissolved with natural silk, casein, albumen, etc.

Dr. Todtenhaupt has described the following process by means of which he produces artificial silk : To 100 grms. (about 3½ ozs.) of pure casein in powder, mixed little by little with 300 grms. (10½ ozs.) of water, are added 20 grms. (308 grains) of liquid ammonia at 10 per cent. The whole is heated until a clear solution is obtained, and then precipitated in an acid bath. According to a more recent process, the same inventor first treats the casein with an alkali, and then dissolves it in alcohol ; by this method he obtains solutions of great viscosity.

H. Timpe, of Amsterdam, relates to a process for the manufacture of artificial silk from milk. A solution of a pyrophosphoric salt is slowly added to the milk, which curdles and forms at first into a jelly-like mass. After standing for a short time the solid materials separate out sufficiently from the whey, so that a separation of the two is possible, and after the liquid present has been pressed out, the product is converted into a tough plastic mass by adding a small amount of ammonia or other alkali. The purified product is freed as much as possible from moisture by pressing, and the resulting powdery substance treated by pouring liquid ammonia on it and kneading until it begins to become transparent. The superfluous ammonia is then poured off, and the mass is allowed to stand in a closed vessel at normal temperature, whereupon it becomes completely transparent and glossy. This material, which can be drawn out into the finest threads, is worked in a well-known manner, and hardened by the action of formaldehyde or other hardening agent.

In the manufacture of artificial silk several points must be considered—*e.g.*, the coagulation of the fluid, the fixing of the coagulated mass, the preservation of the softness of the finished thread, and the prevention of the sticking together of the separate threads. According to a patent by Dr. Y. C. Hartogs, of Amsterdam, these four objects are effected without the use of different vessels for the reception of the different liquids by the employment in one bath, first of a liquid to separate the cellulose rapidly, and then of a different liquid less rapidly precipitating than the first liquid, and adapted to make the coagulated thread non-adhesive,

and which is little, if at all, miscible with the other. In Fig. 98, A is the vessel containing the viscous liquid, and B are the spinning nozzles or spinnerets, from which separate threads C issue ; H is an aqueous liquid, J is a liquid heavier than H, such as nitrobenzine, chloroform, carbon tetrachloride ; and K is a liquid such as benzine or ether, which floats upon the liquid H. The separate threads C coagulate in their passage through the liquid H ; they then pass through the liquid J, in which they are combined to a single thread C^1 near the roller R. After passing under roller R, the combined thread C^1 returns through liquid H, and finally through liquid K, in which it is washed.

Paul Girald, of Lyons, consulting engineer to the Viscose française, is the inventor of a number of processes relative to
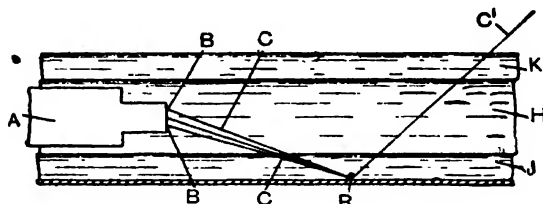
FIG. 98.

this manufacture. In one of his later patents he refers to an improved process for the production of artificial fibres in which are used filaments of cellulose of a determined and constant length, and of a fineness which may attain half-denier. These filaments are wound in groups on spools, which are then cut through along generating lines of the spools, so as to yield a fleece or sliver formed of parallel filaments ready to be subjected to the processes of roving and spinning.

Dr. L. Lilienfeld, Vienna, Austria, has a process for the manufacture of viscose (cellulose-xanthogenate poor in alkali) in which cellulose or a material containing cellulose is treated with caustic alkali in the proportion of not more than twenty-five parts by weight of alkali to 100 parts by weight of cellulose, the product obtained being treated in the ordinary way for the production of viscose.

The Glanzstoff Fabriken Company has a process for the manufacture of stable viscous cellulose solutions, characterized in that cellulose, pure or in the form of oxycellulose, or waste

from the manufacture of artificial silk, is subjected to the simultaneous action of concentrated formic acid and phosphoric acid.

For coagulating viscose Dr. Brandenberger, Thaon-les-Vosges, France, has a process by soluble thiosulphates, such as those of soda, potash, ammonia, etc. The action of thiosulphates on viscose takes place at the ordinary temperature, but the speed of the action increases if the temperature is raised. In addition to their coagulating property, thiosulphates are excellent solvents for alkaline polysulphides, which form impurities in viscose. All alkaline thiosulphates may be used, but sodium thiosulphate is preferable on account of its cheapness. As an instance of a suitable coagulating bath, one part of sodium thiosulphate with five equivalents of water, $Na_2S_2O_25H_2O$, is dissolved in one part of water at a temperature of 50° C. (122° F.).
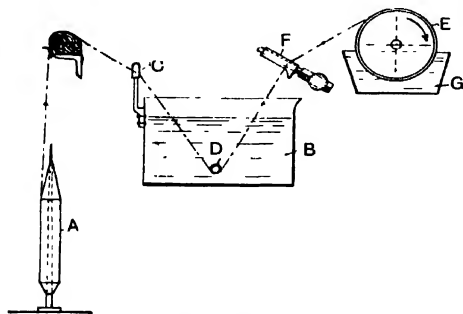
FIG. 99.

Another process for the production of a thread imitating silk consists in coating a thread of, say, 120's to 200's cotton with a layer of lustrous artificial silk similar to the lustre of silk. The thread from the cotton cop A, Fig. 99, is passed over a rod as shown, through a thread guide C, and then through a second thread guide D in the liquid. On emerging from the liquid it passes through a third thread guide F and on to the bobbin E, which rotates in a coagulating liquid G. The thread guide F consists of two arms covered with india-rubber, and these arms may be opened or closed at will by a little screw, like the arms of a pair of compasses ; this arrangement provides means for regulating the thickness of the layer which coats the threads. The liquid B, which imparts the lustre, may be a solution of cellulose, such as viscose, or it may be a varnish. Coagulating bath G is employed only for the cellulose solution. This process, which has been studied in the factories of Chardonnet and by those who work the cuprammonium process, has not yielded practical results ;

la viscose de Stettin alone has been able to manufacture a sort of artificial hair. Despeissis, who follows the cuprammonium process, had already claimed this process in his patent of 1890.

There is still another process of manufacture, the operation of which resembles very much the method of turning as practised in engineering shops. For this purpose hollow cylinders, termed calenders, are employed ; these are heated and coated with a layer of collodion mixed with starch. When this coat is dry, another is applied, and so on until the desired thickness is obtained. These cylinders are then placed in a lathe and rotated, during which time a steel tool removes the substance in the form of an endless shaving or thread, which is wound on to a bobbin as it is detached by the turning tool. If the threads are desired to be coloured, the colouring matter may be added to the collodion.

M. Weertz, of Bradford (British Patent No. 10,211), winds the threads from the spinning bobbin directly on to reels, and these reels, which are specially constructed for the purpose, are then placed into the acid and other baths. The silk is dried and twisted directly without previously winding it on to small bobbins.

According to an American patent, J. Foltzer spins the artificial silk on bobbins or reels, removes the hanks from the reels, and then makes them up into little parcels. The copper is then removed, and the substance washed and bleached in a hydro-extractor specially constructed for the purpose. The copper is removed as follows : Before introducing the acid, the hydro-extractor is rotated sufficiently fast to enable the centrifugal force to prevent the thread from shrinking under the action of the acid of the copper-removing liquid. The silk is then dried on wooden rails.

F. and H. Mitchell, of Bradford, speak of a yarn manufactured from artificial silk waste, and built up of short lengths of single fibres of artificial silk twisted together, and not of continuous lengths of fibre twisted together, as is usually the case in artificial silk yarns. The waste is treated on a Garnetting machine, then passed through gill boxes, combed, and afterwards drawn into a uniform sliver, if such be desired, and then spun, preferably on a flyer frame. It is claimed that the resulting yarn has a much softer appearance and handle than are usually found in artificial yarn. It is also

possible by the present invention to produce a yarn of artificial silk blended with other natural fibres, as opposed to yarns formed of threads of artificial silk twisted with threads of natural fibres.

Müller and Wolf, of Turn-Teplitz, Bohemia, conduct the manufacture of artificial silk and similar cellulose products from vegetable fibrous materials, a process which has for its object the utilization of a solution of bast sheath fibres obtained from hop runners. This solution yields a product of flexibility and lustre which is difficult to distinguish from natural silk.

Much has been said of late of a process for the manufacture of a cheap lustrous thread, the chemical treatment of which is based upon that which has been employed for some time on flax fibre for cleaning it and making it supple. For this purpose the flax fibre is simply passed through a fermentation bath to which has been added a quantity of glycerine, and afterwards passed through water. This treatment costs only one franc per kilogramme (4½d. per lb.), and since the fibre is not injured by the process, it follows that its strength and elasticity are preserved, and the resulting fabrics possess a silky appearance. Since there were at one time approximately 4,300.000 acres in Europe under flax cultivation, and therefore probabilities of reaching, or even exceeding, this area under satisfactory conditions of peace, it would appear that there is a great future for this new process, the secrets of which are carefully guarded by the inventors.

The invention of Carl Gebarrer, Charlottenburg, Germany, consists in treating the artificial silk manufactured from collodion and indiarubber with albumen, and coagulating the matter by means of steam under pressure simultaneously with the process of vulcanizing the indiarubber.

M. Weertz, of Bradford, has invented improvements in making cellulose solutions in the manufacture of artificial threads, the object being the making of a cellulose solution from materials that will allow of the cellulose solution being spun to very fine counts. The invention lies in the employment of the fibres obtained from a so-called silk-cotton family —viz., *Bomboceae*—the fibres of which are largely used at the present time for stuffing pillows, cushions and the like.

Artificial silk threads have for some time been made from glass in a viscous state. This process, however, has never been employed on a large industrial scale. A more recent

process, however, refers to the probability of an industrial value being given to this idea and to the experiments.   The new silk thus obtained would be made from filaments of threads having a diameter of only one-eighteenth of that of an average human hair.   By the addition of different chemical products to the glass mass it is possible to obtain, according to the inventors, a thread of great lustre, strength and flexibility.   The product may, as is the case with the other artificial silk threads, be employed for lace making, weaving, etc.   The pre-war cost price of the threads would be only about 1·50 francs per kilogramme (6½d. per lb.).

CHAPTER XXI

Organization of Staff and Equipment for an Artificial Silk Mill

FOR the production of 350 kgs. (771·4 lbs.) of silk per day, reckoning 27 grms. (415·8 grains) per hour from each distributor, and on the assumption that the spinning, washing and drying departments are kept working continuously night and day, and the preparation, winding, twisting, etc., departments for eleven hours per day, the following are necessary—

```
  1 managing director
  1 chemist
  1 under-manager
  1 book-keeper and accountant
  4 clerks
  1 overseer
  2 men for the washing machine  ⎫
  2 men for boiler               ⎪
  1 man for opener               ⎬ Preparing and bleaching department
  2 men for hydro-extractors     ⎪
  1 man for electrolyzer         ⎭
  1 foreman  ⎫ For the preparation of the copper oxide, the dissolving and
  2 men      ⎭              filtration of the cotton
  1 chief foreman for spinning department
180 men in three shifts (120 men if there are only two shifts) for spinning
       department
 30 men in three shifts (20 men if only two shifts) for washing and soaping
       department
 15 men in three shifts (10 men if only two shifts) for the drying department
105 men for the winding department
 35 boys for the winding department
 80 women for the twisting, reeling, counting, hank cleaning, and packing
       departments
  3 men for the manufacture of ammonia
  2 men for the freezing machine and the compressed-air pump
  2 men for the washing and drying of the silk in hanks
  6 men for the mechanics' and joiners' shops
  5 day labourers
  2 porters and watchmen (in attendance alternately)
  2 firemen
  2 mechanics
  1 electrician
  2 glass-blowers
  1 plumber
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494 employees

At the present time it is usual to reckon one operative for each kilogramme of artificial silk.

HORSE-POWER REQUIRED FOR THE MACHINES

	H.P.
2 compressed-air pumps	8
1 freezing machine	30
2 water pumps	10
2 mixers	6
3 washing machines	7
2 hydro-extractors	10
1 electrolyzer	8
6 spinning machines	15
8 winding machines	16
4 twisting machines	13
4 power reels	4
4 ventilators for spinning department	
5 ventilators for drying department	15
Humidifying apparatus	
Mechanics' and joiners' shops	

Total . . . . . 150 H.P.

When working with soda or potash as precipitating liquids it is necessary to have double the amount of ventilation in the spinning department, in addition to that required by the electrolyzer for the copper recovery, and these combined raise the total by 30 to 40 h.p.

This increase in ventilation is for the purpose of removing the ammonia that is liberated at the precipitating baths, and which, being very slightly mixed with the air of the spinning room, is directly recovered in water. With this recovery object in view, the new spinning machines are boxed in with wood in a similar way to that adopted in the manufacture of Chardonnet silk, where the alcohol and ether are recovered. The doffing of the bobbins is done as far as possible automatically; the bobbins also receive a rapid wash at the spinning frame in order to be able to recover immediately as much of the ammonia as possible. During the manufacturing process, where the spun silk is completely precipitated in baths with large surfaces, the recovery of the ammonia, which is still being liberated, is no longer a simple operation.

	Lamps of 16 C.P.
LIGHTING	
Spinning.	120
Washing, drying, and humidification	50
Winding	70
Twisting, reeling, counting, hank cleaning, and bundling .	100
Preparation and bleaching	30
Mixing and filtration	10

	Lamps of 16 c.p.
LIGHTING—(*continued*)	
Ammonia-making	8
Mechanics' and joiners' shops	10
Machine for washing hanks, electrolyzer, air and water pumps, freezing machine	15
Sulphuric-acid tanks	3
Offices, warehouse, etc.	80
	496

FLOOR SPACE OF THE VARIOUS DEPARTMENTS

	Sq. Ft.
Spinning and washing	11,800
Drying	4,300
Humidifying	3,800
Winding	8,000
Twisting, reeling, hank cleaning, and packing	16,100
Preparing and bleaching	6,800
Mixing and filtration	6,800
Ammonia-making	2,700
Mechanics' and joiners' shops	2,700
Machine for washing hanks, electrolyzer, air and water pumps, freezing machine	4,300
Sulphuric-acid tanks	860
Engine, boilers, and accumulators	7,600
Office and laboratory	1,600
Warehouse, kitchen, dining-room, dressing-room, carriage-house .	13,000
Lodge	550
Total	90,910

CHAPTER XXII

General Notes on the Establishment of an Artificial Silk Mill

It is well known that the existing manufactories are not sufficient to supply the demands. Those who desire to build a factory must first study the different methods of manufacture, which, although resembling each other in many respects, differ from each other in their chemical processes. When it is definitely decided which method appears to be the most advantageous, permission to prosecute the work must be obtained from the corresponding patentees unless the patent rights for such method happen to be public property. Two conditions at least are essential for the success of such a manufactory: (1) A well-equipped factory in a good situation with respect to markets, etc.; and (2) an efficient supply of workpeople under good and capable managers.

The works must be situated near to a constant supply of good and cheap water. The water must be free from lime and other foreign matters which would necessitate filtration or distillation. It is also desirable that a place should be chosen where the waters will not be polluted or used up by the establishment of other industries higher up the stream. There are naturally such dangers when a factory is built on the banks of important or large rivers capable of providing sufficient water for the necessary motive power.

Scheme for the establishment of a factory working with the copper solution, and capable of producing 100 kgs. (220·4 lbs.) of artificial silk per day in an existing building provided with steam or other power up to 50 or 60 h.p., as shown on the following page.

A close examination of the net cost of the various commodities and the selling price of the finished article in the different countries proves irrefutably that this industry is one of the most remunerative. This industry, established under favourable conditions with a simple system, with little delay in installation and a prospect of disposing of the product

without unnecessary delay, is certainly a most favourable one. The complete installation for the production, detailed below and on the following page, amounts practically to 200,000 francs (£7950 approximately). With the pre-war net cost and selling price, or even taking the latter 10 per cent. lower than the lowest market price, there should be a sure profit of 90,000 francs (£3578) with a production of 100 kgs. (220·4 lbs.) per day.

Since 100 kgs. of artificial silk per day or 2500 kgs. (5510 lbs.) per month cost 22,141 francs, or £880, it follows that the net cost is—

$$\frac{22141}{2500} = 8\cdot85 \text{ francs per kilogramme };$$

$$\frac{880}{5510} = 3\cdot2 \text{ shillings per pound}$$

COST PRICE PER KILOGRAMME AND PER POUND OF ARTIFICIAL SILK FOR A PRODUCTION OF 100 KGS. PER DAY, OR 2,500 KGS. (5,510 LBS.) PER MONTH.

	Francs.
Solvent (ammoniacal copper solution)	10,750
Cotton cellulose	1,968
Baths for coagulation, copper removal, and washing . .	3,887
Coal for motive power, lighting, and drying	2,015
Oil and soap	184
Capillaries, bobbins, etc., and spare parts	250

General Charges—

Fire assurance	57
Working accidents	83
Various contributions	140
„ expenses	285
Wages for operatives	3,750
Monthly salaries	2,200
	25,569

By-products to Deduct—

Recovered copper	656
Ammonium sulphate	712
Ammonia recovered directly	1,901
Artificial silk waste :	
1st quality	139
2nd „	20
	3,428
	22,141

ESTIMATED COST OF INSTALLATION OF A WORKS FOR A PRODUCTION OF 100 KGS. (220·4 LBS.) PER DAY.

	Francs.
Installation of plant for heating	3,500
„ „ lighting	3,000
„ „ electricity	12,200
Pulleys and belting	3,350
Chemical preparation	15,700
System of pipes, valves, etc., for works	12,000
Frigorific apparatus	6,950
Large and small air-pumps	5,670
Spinning machines	17,830
Washing and vats	7,240
Winding	4,500
Twisting	9,180
Reeling	7,050
Drying	8,000
Apparatus for recovering by-products	13,000
Glass-making	17,120
Repairing shop and laboratory	9,690
Conveyance of bobbins : foundation and asphalt	5,200
Tanks, pumps, ventilation, and woodwork	25,780
Various unforeseen expenses	13,040
Total	200,000

Or £7,950

Establishment of a Factory for the Manufacture of Chardonnet Silk.—On the hypothesis of a daily production of 500 kgs. (1102 lbs.), about 150,000 kgs. (331,600 lbs.) per year of 300 days' work, the equipment shown on the next page costing approximately 1,012,500 francs (£40,258) will be required. With an additional outlay of 350,000 francs (£13,916) the production could probably be doubled.

Nevertheless, it can be said that certain manufacturers of artificial silk by the nitro-cellulose method, who recover by-products and employ the most up-to-date machines, have been able to reduce the net cost to 12 frs. per kilogramme (4s. 4d. per lb.). A German firm, Johannes Schleu à Beuel, some time ago reduced by 50 per cent. the expenses for solvents by employing a mixture of ethyl alcohol and benzene (German Patent No. 259,241). It is expected that this economical method will encourage the manufacture of artificial silk in Germany by alcohol, a process which had been partially abandoned because of the very high cost. It is too early to be able to state definitely as to the commercial value of this silk.

14—(5265)

	Francs.
Ground and buildings	200,000
Motive power and boilers	75,000
Electrical installation	35,000
Machines and Apparatus—	
Room for mixing the acids	28,000
,, for steeping	4,500
,, for presses and accumulators	20,000
,, for machines for washing cotton	15,000
,, for hydro-extractors	4,500
Manufacture and filtration of collodion	80,000
Spinning	60,000
Silk throwing	50,000
Hank cleaning	2,000
Lustring	4,500
Room for compressed-air pumps	25,000
Denitration	10,000
Interior management of dryers	6,000
Installation of solvents	4,000
Shafts, pulleys, and transmission	16,500
Ventilation	7,500
Electric motors for transmission, and for the machines,	
ventilators, and pumps	45,000
General heating	30,000
Distribution of water	30,000
Unforeseen costs	10,000
Floating expenses for two months	250,000

Total 1,012,500

Or £40,258

Cost price of Chardonnet silk.

	Francs.
Raw material, accessories, and manufacture . . .	8·80
Hand labour	2·90
General expenses	1·85

Francs pr kg. . . . . 13·55

13·55 francs per kilogramme, or 4s. 10¾d. per pound.

The net cost of viscose silk is somewhat as follows—

	Francs.
1. Raw materials	2·40
2. Hand labour and management	3·20
3. General expenses	2·65
	8·25

8·25 francs per kilogramme, or 2s. 11¾d. per pound.

Certain works claim to be able to manufacture the silk at frs. per kilogramme (2s. 6¼d. per lb.), which appears very ɔw when compared with the above. The artificial silk made

from casein is much cheaper still, and a number of other products, as, for example, those of Donard and Labbé (French Patents 320,027 and 388,097), to which the inventors have given the name " Maisin," because the raw material from which they are made is maize, yield artificial products at a minimum cost price. It is almost certain that the artificial silk of the future will be made from a combination of these cheap products—which when employed alone yield an inferior quality of silk—with a solution of cellulose in copper oxide or with a viscose solution.

CHAPTER XXIII

Distinctive Characteristics, Properties and Uses of Natural and Artificial Silks

UNDER the microscope the silks obtained from cellulose are amorphous threads, and have no central canal.

Immersed in sulphuric acid and iodine they give a blue coloration which is characteristic of cellulose. Cuprammonium liquor dissolves almost instantaneously the cellulose silks, whereas vegetable fibres first swell, and require a little time to dissolve. All artificial silks made from nitro-cellulose give a blue coloration when treated with diphenylamine in presence of sulphuric acid. An ammoniacal solution of nickel dissolves natural silk, whereas it has no effect on artificial silk. The reaction is also good for quantitative analysis.

It is known that the liquid secreted by the silkworm is composed of a species of fibrin or special albuminoid material, which has received the name of "fibroin," and a kind of gluey or starchy matter called "sericin," which covers the fibroin. The sericin imparts to the natural silk an aspect rather dull and only a little silky; it is only after the process of degumming that a lustrous and supple thread is obtained. With this known fact in view, several inventors have attempted to produce a substance identical with the fibroin, and to employ this substance to produce an artificial silk thread of the same constitution as natural silk. Satisfactory results, however, have not yet been achieved. Amongst other processes we may mention that by R. Baumann, of Gavirate, Italy, and G. Diesser, of Zurich, Switzerland. These inventors dissolve 100 grms. (1540 grains or, approximately 3½ ozs.) of albumen, preferably that from eggs, in 99 grms. (1524·6 grains) of concentrated formic acid, and afterwards add about 0·1 grm. (1·54 grains) of glycerine diluted with concentrated formic acid. On evaporating the liquid, the inventors state that transparent and elastic pellicles are obtained. The same or similar solutions may be used for the manufacture of artificial silk. Instead of using albumen of eggs, Baumann and Diesser claim to be able to obtain astonishing results by using as raw material the intestines or other membranous

parts of animals containing fibroin in large proportions. These membranous tissues are first submitted to a slow action of formic acid, employing only a minimum quantity of acid to produce a swelling of the membranes, and afterwards promoting a complete solution by a supplementary and proper addition of formic acid. Other inventors have proposed employing acetic acid instead of formic acid.

The different processes that have been mentioned have for their aim that of imparting the appearance of natural silk to artificial silk—that is to say, to cover the artificial silk product with a kind of varnish prepared from fibroin or from lanegenic acid, substances made from silk waste or wool dissolved in alkalies.[1]

Messrs. P. Follet and G. Ditzler, spinners, Verviers, have devoted a considerable time to this process, and have patented the following—

No. 203,196 of 15th October, 1907. A process of treating artificial threads obtained from solutions of cellulose or other analogous substances in an ammoniacal solution of a salt or metallic oxide.

No. 189,814 of 2nd February, 1906. A process of regenerating silk.

No. 190,636 of 27th February, 1906. The dissolving of textile matter and its application.

No. 192,328 of 8th May, 1906. A process of obtaining products as pure fibroin.

No. 195,233 of 16th October, 1906. A process of making threads in the form of pure fibroin.

No. 195,477 of 26th October, 1906. A process of treating spinnable solutions of fibroin, cellulose and other analogous substances.

No. 195,495 of 27th October, 1906. An improvement of the process described in No. 195,233.

Properties and Constitution of Artificial Silk.—The specific gravity of artificial silk from collodion is 1·49 (according to a report issued by Chardonnet in 1889, No. 108, p. 962) ; of raw silk, 1·66 ; of boiled silk, 1·43. In "La Faerber-Zeitung de Lehner" (a journal by Lehner), 1894–95, pp. 49 and 50, Herzog gives the specific gravity of Chardonnet silk as 13 per cent. higher than that of natural silk. According to Silbermann

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[1] *Association des Chimistes Belges,* séance du 20 février, 1901.

(see his work " Die Seide," 1897, Vol. II, p. 148), Lehner's silk should be from 7 to 8 per cent. heavier than natural silk.

" La Oesterreichische Chemiker Zeitung " (1900, p. 269) gives, according to Hassak, the following specific gravities—

Natural silk	1·36
Pres de Vaux silk (Chardonnet)	1·52
Fismes silk	1·52
Walston silk	1·53
Glattbrugg silk (Lehner)	1·51
Glanzstoff silk	1·50

The same journal, " Oesterreichische Chemiker Zeitung," states on p. 268, 1900, that the degree of humidity of the different kinds of silks, determined by Hassak, at 110° to 115° C. (230° to 239° F.) is—

Natural silk	8·71% of water
Pres de Vaux silk (Chardonnet) . . .	11·11% ,,
Fismes silk	10·92% ,,
Walston silk	11·32% ,,
Glattbrugg silk (Lehner) . . .	10·45% ,,
Glanzstoff silk	9·20% ,,

In that part which deals with Chardonnet silk we have given a table which deals with the strength and elasticity of nitro-cellulose silk compared with those of natural silk.

The result of the experiments made by Messrs. Strehlenert and Westergeren on the strength of different silks is given in the chapter on viscose. According to the " Faerber-Zeitung de Lehner " (1894–95, pp. 49 and 50), Herzog gives the following results in relation to Chardonnet silk—

Count.	Strength.	Elasticity.
60 deniers . . .	69 grms. .	155 mm. per metre
65 ,, . . .	83 ,, .	171 ,, ,,

The thickness of the filaments of artificial silk has been determined by Massot (" Leipziger Monatsschrift für Textil Industrie," 1902 and 1905)—

	In Air.	In Glycerine.
Nitro-cellulose Chardonnet silk . .	28·8 μ .	29·4 μ
Glattbrugg silk	35·4 μ .	31·4 μ
Glanzstoff silk	29·5 μ .	28·8 μ
Viscose silk	30·51 μ .	35·45 μ
Natural silk	15·0 μ .	—

The Greek letter μ represents the unit measurement in microscopic researches ; it is termed " micron " or " micro-millimétre," and is equal to a measurement of 0·001 millimetre.

Consequently, in the above table 28·8 μ = 28·8 × 0·001 = 0·0288 mm., and so on for all the other numbers.

The thickness of the artificial silk filament increases in water from one-third to one-fourth of its original diameter. The specific gravity of cuprammonium artificial silk is greater than either Chardonnet silk or viscose silk. This fact is often taken advantage of in comparing the two kinds to the detriment of the Despeissis and Glanzstoff silks. The covering power of the cuprammonium silk in weaving is stated as being inferior to that of the nitro-cellulose threads or the viscose threads. Also the length of cloth that can be obtained from a given weight of cuprammonium silk is less than that which can be obtained from the same weight of Chardonnet or viscose silk of the same diameter.

Dr. Thiele obtained a better cover with an artificial silk made from a large number of very fine filaments. J. Foltzer has also studied this side of the question, and has made efforts to obtain a greater covering power in the following manner : Instead of forcing the solution through ordinary capillary tubes with round section, he produced filaments of a ribbon form by using spinnerets with rectangular orifices. The twisted threads obtained from these ribbon-shaped filaments are approximately equal in strength and in count to the same quantity of circular-shaped filaments, but the rectangular ones occupy more space and consequently the same count of twisted threads appears thicker. The covering power of these threads in weaving is therefore greater, and there is an apparent change of specific gravity. Many difficulties are encountered, however, when this idea is put into practice. First of all, the construction of the capillaries with the actual size of rectangular orifice is a difficult task, and the filaments precipitated through these orifices are found, when examined under the microscope, to be more or less round or oval instead of like a ribbon. This irregularity in form proceeds from the contraction which the thread undergoes in the precipitation, and especially in the copper removal process—a contraction which is greater when the precipitation is performed by concentrated and warm alkalies than by acids. In order to obtain ribbon-shaped filaments it appears necessary to use capillaries with concave openings somewhat similar to the shaded part in Fig. 100 and to calculate the two ends A B and C D of the opening so that the section of the filament

will be rectilinear after the effect of contraction due to the processes of precipitation and copper removal. A still greater difficulty would be experienced in the making of the capillaries with such openings unless one employs the process practised by Lehner or Thiele with capillaries having large openings. The upper part of Fig. 101 illustrates four different sections of capillaries, and at A to D are shown the resulting sections of threads formed by each opening after taking into account the shrinkage which the thread undergoes during precipitation and copper removal. A filament that approaches most closely the shape of a ribbon is therefore produced by a capillary tube with an orifice similar to D. Artificial silk formed with ribbon-shaped filaments reflects light brilliantly and uniformly,
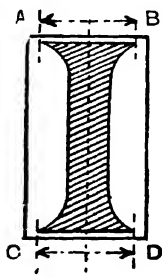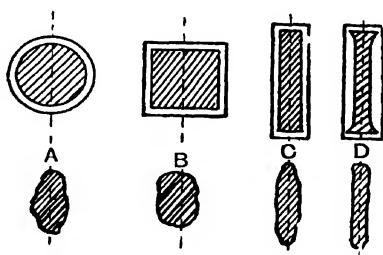
Fig. 100.   Fig. 101.

and is free from the scintillations and irregular reflections that are emitted from silk with round section. This effect of light reflection is exactly the same for the thick threads of artificial hair according as they are made from round or rectilinear orifices.

The first coagulation of the threads as they emerge from the capillaries is only superficial ; an outer membrane is formed on the partially formed thread, and this membrane prevents the precipitating liquid from penetrating into the heart or centre of the thread, where the substance is still in a liquid state. The complete precipitation takes place only after a determined time, which naturally depends partly upon the count or thickness of the thread and partly upon the concentration of the precipitating liquid. Somewhat similar conditions obtain in the copper-removal bath. During the processes of precipitation, copper removal and washing, an expulsion

of air, ammonia and other products from the threads takes place—an expulsion which appears to form artificial cells in the threads. The greater part of these cells disappears, however, during the contraction and the tension which take place during the drying process. These cells are especially visible during microscopic observations on threads which have not yet been dried a first time.

It would be interesting to follow a thread in its formation during the stages of drawing by the Thiele process, for here also is necessarily formed in the first place an exterior membrane. The drawing-out process must also be imparted to this skin or membrane which is already formed on the partially or imperfectly precipitated inner portion, and it would appear at first sight that such a process would not be favourable to the quality of the thread. By this statement we desire to say that the structure of the thread precipitated in stages and in different technical conditions cannot be uniform, and that filaments as fine as those of Thiele, but precipitated directly and without any draft, must be stronger and the structure more uniform than are those which undergo a draft during precipitation. Let us add, however, that the above remarks are only suppositions, for up to the present no means, other than that of drawing, have been found to make such fine filaments.

By precipitating with acids, a fibre is obtained with a constitution which is weaker, less compressed, less impermeable to water, but on the contrary more supple, than those threads which are coagulated in alkalies.

Property and Durability of Threads.—The first lustrous artificial fibres were made to satisfy the general tendency which always exists in the manufacture of cheap products in imitation of more superior and expensive ones, and originally very inferior goods were placed on the market, but these were not very successful.

The artificial threads, however, which are manufactured at the present time resist very well the natural agents of decomposition. The deterioration of artificial silk threads has been especially prevented by the elimination from the fibres of all chemical agents used as solvents, precipitating agents, etc., and so leaving practically only pure cellulose. Afterwards precautions were taken in the course of the various manipulations with regard to cleanliness to avoid stains appearing on

the silk ; attempts have·even been made to impregnate the fibres—as has already been done with natural silk—with a substance capable of paralysing the phenomenon of oxidation which accounts for the alteration. Researches in this line have been specially made by Dr. Meister in Switzerland, and by Gianoli, of La Société de Conditionnement de Milan, who impregnated the silk in sulphocyanic acid or in a derivative of this acid.

The silk threads are kept preferably in a dry and aired place, but, curiously enough, it has been remarked by several manufacturers that artificial silk which has been kept parcelled up in the warehouse for several months has a better appearance than silk which has just been spun. It would appear, therefore, that the silk improves under such conditions. It is naturally impossible for us to speak about those works in which experiments are proceeding, and where the products are being improved from month to month.

This slight modification, although advantageous with respect to the appearance of artificial silk, must be the effect of some previous decomposition of the cellulose, for it is evident that no structure, natural or artificial, is permanent. This process of decomposition, if such a term may be given to this slight modification of the fibre, may sometimes be due to insignificant traces of chemical products that remain in the threads, and which produce some feeble disorganization, or which escape in gaseous form. The modification might equally be due to a special unknown form of fermentation, which has an effect upon the thread only under certain conditions and for a certain time after the thread has been spun, for after a time the silk seems to enter into a more stable state. This change takes place in those threads which are made by the cuprammonium process ; we are unable to say whether similar conditions obtain with Chardonnet, Viscose, and "Celanese" silks. The above are only general features from several observations, and in more conclusive researches it would be necessary to take into account the action of the oxygen of the air, the temperature, the hygrometric state of the room or warehouse, and to ascertain if there are other factors which exercise an influence on the threads.

Of all textile products artificial silk has been in use for the shortest time. Textile treatises have mentioned it for only fifteen to twenty years, whilst natural silk formed the basis

of an important industry in very remote times. Similarly, wool, cotton and linen have been used continuously for very long periods, and even jute was made the basis of a large industry more than sixty years ago. With the introduction of the power-loom, and the extraordinary progress of mechanical invention, the development of the cotton industry was phenomenal, and one might expect a great development of the artificial silk industry, and especially in connection with all these different applications of cellulose which are perfectly adapted to the requirements of modern industrial processes. The improvement in mechanism, the simplified chemical processes, and the new properties of manufactured products, cannot fail to contribute to a considerable development in this particular industry.

APPROXIMATE ANNUAL PRE-WAR PRODUCTION OF RAW MATERIAL FOR TEXTILES

Kind of Material.	Weight of Raw Material.		Weight Transformed into Threads, Reduction made for Waste, Grease, Sand, and other Impurities.	
	Kilogrammes.	Tons.	Kilogrammes.	Tons.
Cotton	4,600,000,000	4,527,336	4,250,000,000	4,182,865
Wool	1,000,000,000	984,203	500,000,000	492,102
Natural silk comprising cocoons	114,000,000	112,199	25,000,000 14,000,000 waste	24,606 13,779
Artificial silk—				
Nitro-cellulose	—	—	1,600,000	1,575
Cuprammonium silk	—	—	1,350,000	1,329
Viscose silk	—	—	550,000	541
Jute	—	—	1,500,000,000	1,476,365
Linen	—	—	500,000,000	492,102

The Employment of Artificial Silk Threads.—After having seen one by one the different phases of the artificial silk industry, of which the first years were attended with considerable difficulties, we may now mention the particular uses to which these threads are put. The threads, as such, are used greatly in the manufacture of lustrous and light ribbons. In Lyons, muslins in hair and artificial silk are manufactured ; unbleached artificial silk tissues to be dyed in the piece ; the artificial silk is also used in the manufacture of certain types

of guipure and other lace. The industry, however, which up to a few years ago utilized the largest quantity of artificial silk and hair is that which is responsible for the manufacture of galons, braids, tresses, and different kinds of trimmings. Even in embroidery the artificial threads have played an important part during part of the last decade. In Lyons and district alone the value of the fabrics made from artificial silk amounts to approximately 500,000 francs (£19,800) in twelve months. The employment of these artificial threads and hair is being extended more and more, and the products are disposed of comparatively easily and with a reasonable profit.[1]

[1] A considerable amount of artificial silk yarn is now knitted into all kinds of ties, scarves, hose and garments, while large quantities are woven into various kinds of fabrics.—*Transr.*

CHAPTER XXIV

Dyeing
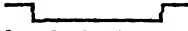
First of all it should be stated that colouring matters or dyes constitute a class of substances with a definite and determined constitution ; they are obtained synthetically—in numerous cases quantitatively—by the reaction of constituent groups, whereas the constitution of both natural and artificial fibres is problematical, and the artificial ones vary according to the kind of cellulose employed as raw material. We do not propose to give a detailed description of dyeing, but simply a very superficial account of the general methods employed.

Dyes are solutions of colouring matter transferred and solidified on the outer walls, and to a certain extent in the interior of the fibrous substance or artificial silk thread. This more or less homogeneous distribution of the colouring matter in the mass to be dyed is, according to Cross and Bevan, an osmotic effect, and also a constitutional relation of the fibrous substances to the colouring matter. Chardonnet silk exhibits a very great affinity to basic colouring matters, whereas cuprammonium silk and viscose silk are dyed best with substantive dyewares. In general the behaviour of artificial silk to colouring matters is similar to that of cotton, with this difference, that the artificial silk fibre, being a hydrocellulose, has a greater affinity for dye than has cotton cellulose. It follows naturally that for equal amounts or weights of the two substances, the artificial silk requires the smaller quantity of dyeware. Chardonnet silk is dyed perfectly with basic dyes without mordanting, whereas the dyeing of cuprammonium and viscose silks is, like that of cotton, preceded by a mordant bath of tannin or tartar emetic. The artificial silk remains for two to three hours in the mordanting bath at a temperature of 50° C. (122° F.), and, according to the depth of shade required, one uses—

2 to 5 per cent. of tannin and
1 per cent. of hydrochloric acid,

calculated on the weight of the material to be dyed. The hanks are then removed from this bath, and after the excess liquid has been extracted, they are left for twenty minutes

in a cold fresh bath to which is added from 1 to $2\frac{1}{2}$ per cent. tartar emetic, or a salt of antimony. Finally the hanks are rinsed or else left to drain.

Chardonnet silk is weaker when wet, so that the dyeing of this substance must be conducted with great care, and the work performed by careful and experienced dyers. Unless this is done there is a danger of the threads losing all their elasticity in the moist state, and the hanks being broken and ruined when taken from the dye-vats. The hanks of artificial silk which are to be dyed direct in one operation are suspended on very smooth rods such as bamboo canes or else on ⌐‾‾‾‾‾‾‾⌐ shaped glass rods. For the light shades the bath is heated to 40° to 45° C. (104° to 113° F.), and for the medium shades to 50° to 55° C. (122° to 131° F.). The heating is done with advantage with a steam coil at the bottom of the vat, and this coil is separated from the material by a perforated false bottom through which the liquid may freely circulate. From 0·25 to 0·30 per cent. of caustic soda and an equal quantity of Glauber's salt (sodium sulphate) is added to the dye. If brighter results are desired the caustic soda is replaced by the same quantity of sodium phosphate. Several dyers obtain equally good results by adding to the dye-liquor special oils and soaps for dyeing. The dyeing is continued for three-quarters of an hour for light shades, and for $1\frac{1}{4}$ hours for deeper shades. During the operation of dyeing, the hanks, as in all other branches of dyeing, should be repeatedly turned in order that the colour may be uniform.

If the colour of the silk is not so deep as that of the pattern after one hour's dyeing, it is necessary to withdraw the hanks from the vat, augment a little the strength of the liquor, thoroughly mix, and then continue the operation of dyeing for twenty to thirty minutes. When the dyeing is completed, the hanks are carefully washed or rinsed in another vat, allowed to drain and then covered with a kind of scrim cloth or muslin. The latter protects the material, and also allows the water to be driven out in the hydro-extractor or other apparatus. Finally, the artificial silk is dried in ventilated rooms kept at a temperature of 40° to 45° C. (104° to 113° F.). In order to make the silk flexible it may be plunged, before dyeing, into a bath containing a small quantity of Marseilles soap or monopole soap and at a temperature of 50° to 60° C. (122° to 140° F.). It is hardly necessary to mention that for

dyeing purposes the water should be as soft as possible—*i.e.*, free from lime and iron ; many dyers use water in the form of condensed steam.

In order to obtain a beautiful and dense black, it is necessary that the operations of dyeing should extend over three to four hours ; during the first half of the time the temperature should be at 45° C. (113° F.) and for the second half 65° C. (149° F.).   Originally, the silk made from acetate of cellulose was more difficult to dye than the other artificial silks, but " Celanese " silk is now easily dyed by the S.R.A. dyestuffs. Since artificial silk is composed only of cellulose, it might be thought that, in virtue of the homogeneity of this substance, the most delicate and evenly dyed shades and tints could be obtained.   Unfortunately, this satisfactory condition can result only when the thread is strictly uniform in count, and it may be remarked that the greatest difference in colour obtains when the yarn of the same hank varies most in thickness.   The unequal shade in such cases is due more to this irregular thickness of the yarn than to any imperfection in the dyeing ; the various manufacturers have, however, made considerable progress in avoiding this defect.

The Conversion of Cellulose into Artificial Hair, Thread, Ribbons, Felt, Leather, Films, Wall Decoration and Cloths for Flowers, Bookbinding, Waterproofing and Ordinary Textures

THE MANUFACTURE OF SIMILAR PRODUCTS, AND APPLICATIONS OF CELLULOSE.—The net cost of artificial silk is influenced more by the wages of the operatives than by the cost of the raw material and the necessary chemicals for transforming the latter into a saleable article. The larger quantity of manufactured artificial silk is only of second or of third rate quality, and realizes comparatively low prices ; similarly, the waste is not very valuable, and hence it has to be sold cheaply. These three lots embrace from 40 to 45 per cent. of the total net cost. It is the hand labour in the spinning, the various washings, winding, twisting and reeling, coupled with the extended time which these processes demand, that accounts for the high net cost. In order to reduce the cost of handling, and also to prevent waste, several manufacturers and inventors have made efforts to obtain not only a continuous thread of indefinite length, but also to produce an artificial sliver which is then, alone or in conjunction with certain ordinary textile fibres, carded, combed and spun by any of the well-known methods. This artificial sliver is designated " artificial silk waste," " schappe artificielle," " schappe nouvelle," or " schappe imitat," according to the district in which it is manufactured or to the ideas of the inventors. The industry concerned with this imitation product is relatively new ; nevertheless, artificial silk waste from bobbins and from defective hanks has been utilized from about the year 1910. This material is cut up into lengths of from 10 to 20 millimetres (say, 4 ins. to 8 ins.), and mixed with cotton, wool and other textile fibres to be ultimately spun into a mixed yarn on self-acting mules, ring spinning or other frames. We have already had occasion to mention such a process— that of Messrs. F. and G. Mitchell, Bradford, British Patent No. 29,030, 1911—in which artificial silk waste is used alone or mixed with other textile fibres.

Paul Girard, engineer, of Lyons, was probably the first to manufacture directly this artificial silk waste. In his French Patent No. 438,131 he states that up to the present continuous threads only have been spun from artificial silk, and a number of these threads have afterwards been twisted together so as to obtain a thread which should resemble natural silk as much as possible. On the contrary, the present invention has for its object that of producing directly very fine artificial filaments, say, from one to three deniers; these filaments, during their formation, occupy positions practically parallel to each other. This enables the filaments to be twisted directly without having been previously combed. To this end, the artificial silk threads proceeding from any cellulose solution are wound on to a large drum, or on to reels, as the threads emerge from the precipitation bath. The drum or reel is removed as soon as the desired quantity has been wound on, and then the fine filaments on the reel are cut at one or more places in order to obtain parallel fibres of equal length. These filaments are taken to the doubling or twisting machines, where they are treated similarly to cotton or wool.

Paul Girard follows the viscose process in manufacturing these threads, and in his French Patent No. 438,131, he describes the apparatus illustrated in Fig. 102, and by which he realizes his invention in a practical manner. Girard claims to be able to manufacture artificial waste silk for 2·50 francs per kilogramme (10·84d. per lb.). The solution of cellulose is under air pressure in tank A, from which it passes through pipe B into distributor C, and then into the capillary tubes D. These capillary tubes dip into the coagulating bath in trough E, and discharge a very large number of threads F, which, as already stated, are wound on to a large drum or reel G. The drum G is placed in and out of action by the fast and loose pulleys and the series of wheels represented in the diagram. Girard also describes in his patent an automatic arrangement for removing the full drum by empty ones, as well as an apparatus which can be fixed on the drum of silk, and by means of which the silk can be cut into desired lengths.

There are other processes in existence for the manufacture of artificial silk waste. Thus the method adopted by P. Vindrief, French Patent No. 442,015, differs only from that of Girard in that the threads are drawn very fine during the spinning process. The inventor seems to place great importance

on this drawing process, and he has no hesitation in drawing the filament in the spinning, between the capillary tube and the winding drum, to that degree of fineness which immediately precedes the breaking point. The winding and the cutting are practised in much the same way as in the Girard process. P. Vindrier states that his artificial silk waste can be utilized specially in the manufacture of velvet and plush fibres. Up to the present it has not been practicable to use other artificial silk filaments of much higher count.
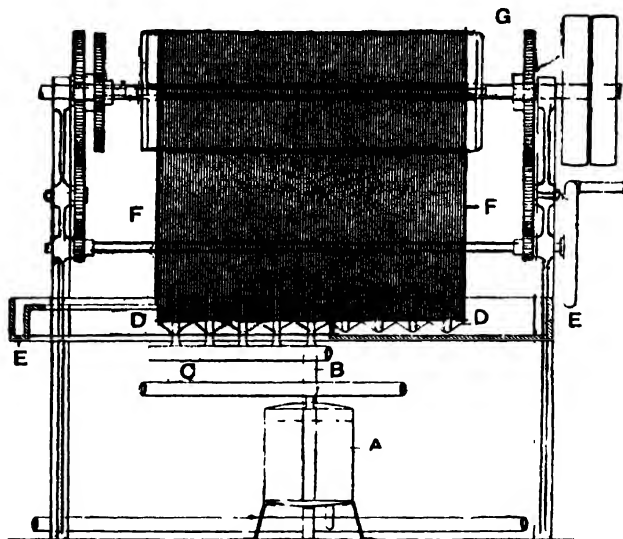
Fig. 102.

Another process, very rapid and capable of great production, is that of A. Pellerin, French Patent No. 442,022. This inventor does not spin his silk on bobbins or reels, but produces a sliver composed of filaments more or less long by receiving the silk at the orifices of the capillary tubes into a moving coagulation bath, and this moving liquid leads the threads away from the capillary tubes and draws them out. This method of drawing has been mentioned long ago by other inventors. In this manner it is possible to produce great quantities of artificial silk sliver with simple apparatus and with a minimum amount of hand labour.

In Auguste Pellerin's Austrian Patent No. 55,749 appear

further details of his process.   The solution of cellulose (viscose) is forced by pressure through one or more filters—for example, very fine metallic cloth.   As the threads emerge from these openings they are received on a very fine endless cloth on which the artificial silk is deposited without consideration of order—not parallel, as in the Girard process.   The material finally drops from the endless cloth into a washing bath.   It is then dried, carded and spun in much the same way as cotton.   A. Pellerin employs for coagulation a sulphuric acid bath diluted to 20° Bé.

Alfred Bloch (French Patent No. 447,068, and Belgian Patent of 18th August, 1911) manufactures a similar product which he names "artificial cotton."   Cleaned and bleached cotton is dissolved in ammoniacal copper oxide, and after solution, the mass is filtered under pressure.   The lower part of the filter—which liberates the artificial filaments through very small openings—is placed on a circular bath which may be put in motion.   This bath is similar to a hydro-extractor, and its inner circumference is provided with very fine pins such as those on card clothing.   The object of these pins is to hold the coagulated filaments and to prevent the partially precipitated threads from sticking to each other.   The precipitation bath is sulphuric acid diluted with water.

Francis Beltzer has published a treatise in Paris in which an interesting arrangement for the manufacture of artificial silk waste is described, when the object is to make, not a continuous filament, but a sliver composed of filaments in any order, and of different lengths, and one which can be combed and spun as are other natural textile materials.   The solution of cellulose arrives by the pipes T and U, Fig. 103, passes through the valve V and the filter X, and then through the pipes Z to the capillary tubes A.   On emerging from the capillary tubes A, the solution, in fine filaments, falls into the coagulating liquid which is supplied through valve R and flows into the conical chamber G.   Here it is whirled round, and, in addition to coagulating the filaments, it carries the latter round and round ; the filaments ultimately drop through the opening B in the bottom of the chamber G.   Both threads and liquid fall on to a revolving drum H, on which the threads are wound under a certain degree of tension.   The drum H, which rotates in the bath K in the direction indicated by the arrows, has also a to-and-fro endlong motion, so that the

threads are, as it were, cross-reeled on the drum.   The coagulating liquid escapes by the overflow pipe L into the reservoir M, and is withdrawn from M by a centrifugal pump N, and delivered into the filtering chamber O, in which are retained the broken filaments which may happen to be carried into the chamber along with the liquid.   The filtered coagulating
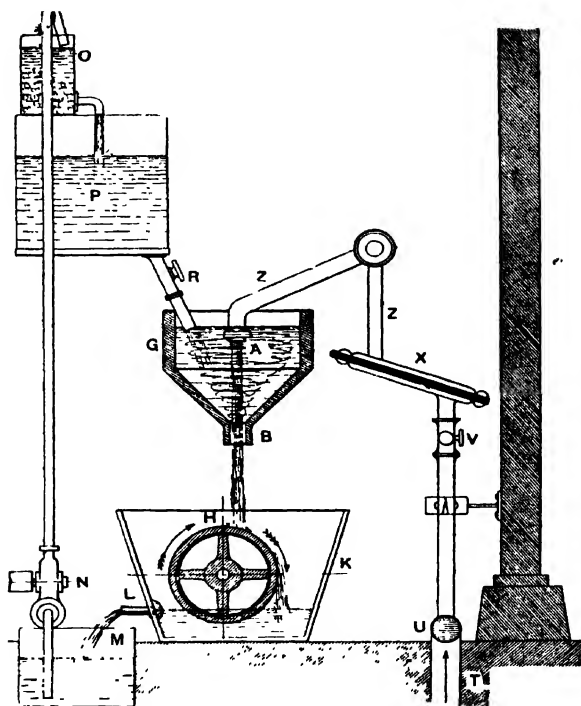

Fig. 103.

liquid flows into the large reservoir P, and is allowed to leave here at the required speed by the valve R into the spinning bath G.   The coagulating bath is therefore circulating continuously, is reinforced in proportion to the degree Bé. required, and is filtered automatically ; it is thus freed from broken filaments or other precipitated matter which happens to be pumped into the filtering chamber O.   The hand labour, even with the high production, is minimized, and there appears to be a future for this method of manufacture.   It is said

that the engineer, Paul Girard, of Lyons, has obtained good industrial results by this method. La Société Franco-Suisse des Textiles Chimiques, of Paris, employs the Girard processes.

Artificial Hair.—Artificial hair has been made for several years in the artificial silk factories. It differs from artificial silk in that it is in the form of a single, comparatively thick, and rigid thread, whereas ordinary artificial silk is composed of several fine and supple filaments. This artificial product resembles horse-hair, which is, as all know, in the form of a round thread, rather thick and not very lustrous.

In 1900 the Kunstseide de Francfort patented a process by which artificial hair, termed " Météore," was made by reuniting, near the capillary tubes, two or more filaments, each of which was thicker than the threads of ordinary silk. This reunion must be made before the precipitation is complete in order that the threads may still be able to adhere to each other, and to form, by their union, a single thick thread which shall resemble that of natural hair. The thread is then denitrated, and treated similarly to threads of Chardonnet silk.

At a later date the Glanzstoff Fabriken imitated this product, for they state in a British patent of the year 1905 that it is possible to manufacture directly artificial hair, to which they give the name " Sirins," by pressing the ordinary solution (ammoniacal copper oxide) through capillaries of 0·5 mm. diameter into caustic soda of 25° to 30° Bé. The other processes —spinning, washing and copper removal—are the same as those employed for artificial silk. It is even possible to spin directly on to reels, wash the hanks, and remove the copper before taking the hanks off the reels. However, seeing that the threads are so thick, it is a good plan to submit the artificial hair to a prolonged treatment in the alkaline coagulation bath before removing the copper. The resulting product is transparent, very lustrous, and possesses a solid appearance. This artificial hair is specially employed in the manufacture of tresses for hats, and also for several fancy textures. It is, therefore, an article of fashion for which the demand will vary ; consequently, it may only be an accessory to the artificial silk manufacturers. Indeed, we know that certain works, which are employed exclusively in the manufacture of artificial hair, have had successful runs for one or two years and then the demand has stopped in consequence of a change in fashion.

Fine hair—*i.e.*, a thread of a thickness between the filament of artificial silk and natural hair—is sold as artificial hair. This product is manufactured in the same way as artificial silk ; it is capable of being dyed, combed and curled, and when a little of its lustre is removed—for example, by B. Borzykowski's patent, in which lead oxide is added to the precipitation bath for this purpose—it may easily be mistaken for natural horse-hair.

Lucien Crespin, of Paris, has described an apparatus for making flat artificial threads. These threads, which are made in the form of narrow ribbons, are obtained simply by employing a capillary with a narrow slit instead of one with a circular opening. L. Crespin uses nitro-cellulose as a base, but these flat artificial threads may be made by other processes. This product is also known as artificial straw.

The firm of Heberlein & Co., of Wattwyl, Switzerland, produces a new kind of fancy threads and ribbons. For the fancy threads they unite one or more cotton threads with one or more threads of natural silk, artificial silk, mercerized cotton, or ramie ; they impart a twist to these threads and coat them with a gluey or gelatinous substance which unites them. This compound thread has, according to the adhesive matter employed, a great reflecting power and a particular scintillation. According to the degree of suppleness required, one may employ as viscous matter, gum, gelatine, collodion, dextrine, or any solutions of cellulose. By employing several threads of different colours it is possible to form a corresponding fancy thread. In order to make ribbons, plain or fancy, the threads are laid parallel to each other, and passed in this condition as a narrow warp through a viscous solution which coagulates them.

J. Foltzer and Ed. Weiss describe in the Swiss Patent No. 37,584, a process for the manufacture of artificial ribbon which is obtained directly by pressing a solution of cellulose mixed with fibres through a narrow slit ; the fibres impart a certain degree of suppleness to the product. After copper removal, washing and drying, the ribbons are ornamented or embossed by means of cylinders, or by goffering, with designs in high and low relief. The product is flexible and very elastic. Rectilinear openings, such as that illustrated in solid black in A, Fig. 104, are utilized to produce artificial ribbons, but if the opening is made of the form illustrated

at B, a ribbon is obtained with a surface which corresponds to a series of thick longitudinal threads ; the result resembles certain artificial straws.

Several inventors have attempted to obtain lustrous threads by coating a cotton thread or other textile thread with a solution of cellulose or of varnish. The results thus obtained have not, however, been very satisfactory. Paul Girard, of Lyons, is amongst them, and in the French Patent No. 430,939 he describes a method by means of which a thread of cotton is made to pass through a pipe at the end of which is a capillary tube with an opening slightly larger than the cross-section of the thread. This pipe contains the cellulose solution (viscose) which coats the cotton thread in its passage with a lustrous layer. Another feature of this patent is that the inventor praises equally well the manufacture of hollow threads. For this purpose he employs a capillary tube in
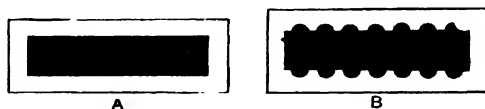
FIG. 104.

the centre of which is introduced a fine wire. This wire, which forms the hollow in the thread, is heated—for example, by the passing of an electric current. The heat from the wire coagulates the solution which comes in contact with it— *i.e.*, the inner portion—while the remainder of the solution is coagulated by means of one of the ordinary coagulating liquids. Paul Girard names his products " artificial straw."

Dr. Y. C. Hartogs, of Amsterdam, has also been occupied with the manufacture of hollow artificial threads, and in his German Patent No. 247,418 he describes an interesting apparatus. Differing from Girard's process, Dr. Hartogs precipitates the exterior part as well as the interior part of the threads by coagulating liquids.

Bernard Loewe, of Paris, has patented a number of ways of coating a thread of cotton or other fibrous material with a lustrous layer of cellulose, and uniting this thread as it emerges from a capillary tube with one or more artificial silk threads spun at the same time. We shall deal with one only of Loewe's processes, but his is practically the complement of

the other preliminary processes, and the result of different attempts. Fig. 105 illustrates the apparatus employed by the inventor. A thread of cotton, natural silk, or other fibre traverses from top to bottom of a capillary pipe that is charged with a cellulose solution, and finally emerges from the orifice A. This natural thread becomes coated with the solution, which adds lustre to it. But it is an interesting fact stated by the inventor that the sectional form of the natural thread to be coated is not absolutely circular, and therefore the thread does not fill the narrow opening completely ; as the thread B emerges, it carries in its train a certain amount of the solution in the form of another thread C. In addition to this there issues from orifice D a thread E of artificial silk, which is joined to the two threads B and C. The final product is therefore composed of three distinct threads—
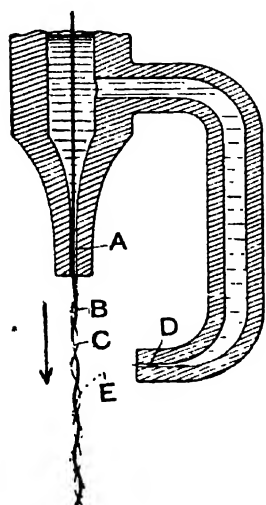
(1) A thread of natural cotton or silk.

(2) An artificial thread formed from the solution which escapes with the cotton or silk thread.

(3) A thread of artificial silk.

The three threads are spun in free air, and allowed to fall as indicated by the arrow into a coagulation bath, not shown. By the simultaneous action of compressed air, which is necessary for spinning, and the tension on the natural thread B, the inventor claims to obtain an artificial

Fig. 105.

thread C of an extreme fineness, and one which has the silkiness of the best natural silk. This thread C, formed as indicated, cannot be perfectly regular, and great difficulty will probably be experienced in practical working, for when a knot or slub, for example, in the natural thread B reaches the narrow part of the capillary tube, it is almost certain to break and to interrupt the process. In one of his patents the inventor claims to be able, by a special treatment, to separate the artificial threads from the natural ones, and to wind them separately on to bobbins. This latter operation does not appear to be very practicable. The numbers of the German

patents of B. Loewe are : 234,927 ; 235,602 ; 238,160 ; and 252,059.

In addition to the artificial silk products in threads, hair and ribbon, there are several other articles made from solutions of cellulose. Thus, in the German Patent No. 106,043, is claimed a method of manufacturing an artificial cloth prepared in the following way : A wide thin film or sheet of cotton fibres is laid on a horizontal surface and is impregnated with a solution of ammoniacal copper oxide. The cotton cellulose is attacked by the solvent, and shortly afterwards the dissolved substance is precipitated by caustic soda or caustic potash, which is poured on the sheet. By this method the fibres of cotton are united to form one continuous sheet from which the copper is removed, and the sheet is then washed, squeezed, dried and compressed ; it then forms a fabric which may be used for linings or other purposes where strength is not important. It will thus be seen that in this old patent is indicated the process of cellulose coagulation by alkalies, and it is only fair to state that the patents for coagulating cellulose by caustic soda and caustic potash, lodged much later by Linkmeyer, Glanzstoff, Meister-Lucius, Foltzer, etc., gave nothing new.

Another process for the manufacture of artificial fabrics, artificial felt and artificial leather, is described in J. Foltzer's French Patent No. 369,402 (German Patent No. 194,506). The principal part of the apparatus used in this process is illustrated in Fig. 106. The cellulose solution tank C is provided with a long slot D and an adjustable apparatus for regulating the size of the slot. The solution is forced through this slot, and drops on to the rotating drum A, which revolves in the cistern B in the direction indicated by the arrow. Three longitudinal scrapers E are adjusted to spread the solution uniformly on the surface of the drum. One or more combined brush and fan chambers N serve to carry short-length fibres—cut specially to a determined length—or pulverized fibres towards the rotating drum A. These fibres adhere to and cover the layer of cellulose solution as it passes the mouth of the chamber N. The layer of cellulose is coagulated in the liquid—say, sulphuric acid, caustic soda, or caustic potash—contained in the cistern B. This liquid hardens the mass, and the fibres are thus securely held on the surface. The combined cellulose and fibre sheet or cloth is

doffed at the point M, carried forward by the two endless cloths G and H, between the rollers P, and finally delivered by the plaiting-down apparatus O into the bath J, where the fabric is treated by other chemical substances. It is washed and then dried under tension. In virtue of the above felting-like process and a final goffering, the product assumes more or less the characteristic features of a fabric ; it is, however, less flexible than an ordinary cloth.
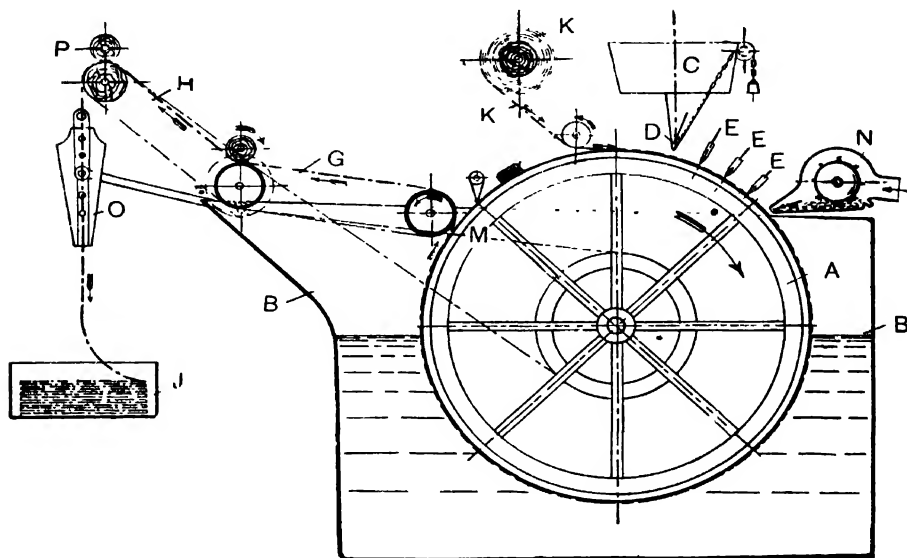

FIG. 106.

According to the description given in the patent, it would appear that both sides of the solution could be made to take on a felt-like effect in one and the same operation. These products, which handle something like parchment, are particularly applicable for wall decoration. More flexible products can be obtained as follows : A viscous mass containing about 8 per cent. of cotton in perfect solution is prepared. To this solution of cellulose is added about 3 to 5 per cent. of vegetable fibres—waste cotton or wood pulp—and the whole mixed until a homogeneous mass is obtained. This substance is then placed in the distributing bath C, Fig. 106, and, by allowing a comparatively thick sheet to pass through slot D

it is possible to make a great width of artificial leather which is very strong and flexible. With the same machine an ordinary fabric may be coated with the cellulose solution. Thus, the fabric may come from roll K on to the drum A, and be coated with the solution at D, and the two are fixed together by the coagulating liquid in vat B. The machine may be used for the manufacture of films by employing homogeneous solutions in which the cellulose is perfectly dissolved and filtered in order to remove all impurities. It is necessary to avoid the formation of air bubbles in the mass, or to eliminate them carefully, to spread the layer very uniformly, and to precipitate perfectly in order to avoid opaque parts and milkiness in the film. The product possesses great solidity and remarkable elasticity ; it is very transparent ; can be easily dyed in all shades ; and when the mass is ammoniacal copper oxide, viscose, or acetate of cellulose, the film is not very inflammable, does not burn so quickly as ordinary cotton, nor does it present the same degree of combustibility as products made from nitro-cellulose. The product can be used as parchment, as an article of decoration, fine boarding, bookbinding, in the manufacture of artificial flowers, transparent films, photographic purposes, etc.

Impermeable Fabrics : Carl Baswitz, of Berlin, causes ordinary fabrics to be passed through a solution of ammoniacal copper oxide in which has been dissolved parchment paper. These tissues are attacked by the ammoniacal copper oxide, and at the same time covered with a layer of more or less impermeable parchment—the whole being formed into a compact body. The product is finally passed into a bath of acetic acid, then neutralized with ammonia, and dried. With suitable treatment the copper in these cuprammonium solutions can be replaced by zinc, and this has been put into practice by Ch. F. Hime and J. H. Hood, of Camden Town, in order to protect the cloths and to make them waterproof. Their method is to dissolve cotton in ammoniacal copper oxide, then precipitate the copper by zinc, taking care not to precipitate the cellulose. They thus obtain a colourless solution of cellulose. In this solution is steeped the cloth to be waterproofed. After this treatment the cloth is squeezed and finally dried on a drum.

Within the last decade viscose pulp and acetate of cellulose have been largely used in the manufacture of films and for

water-proofing fabrics. We may mention, amongst others, the films of the Boroid Company, London ; Lumiere and Planchon, of Lyons ; La Société " Cellon," which employs the Eichengoun patents ; and La Société " Cellophane," at Thaon-les-Vosges.

Artificial Tulle and Lace.—The idea of manufacturing tulle and lace without having recourse to spinning and weaving is not new. In 1899, Adam Millar, of Glasgow, had constructed an apparatus for this purpose. Solutions of cellulose or other viscous substances were forced through capillary tubes on to an endless cloth : this cloth was very fine and smooth, and was rotated at a uniform speed. As the viscous liquid flowed through the capillary tube it hardened. In order to obtain artificial tulle by this process, the capillary tubes were mounted on two or more distributors to which was imparted a to-and-fro movement perpendicular to the direction followed by the cloth. While one distributor moved to the left, its companion moved to the right, and vice versa, so that the combined movements of each pair of distributors and the travelling cloth resulted in the deposition of the solution in ogee forms on the moving endless cloth. The movement of the distributors was adjusted so that the outer edges of each sinuous band joined the outer edges of the neighbouring sinuous bands at regular intervals, became attached, and thus formed an artificial tulle with regular meshes. According to the nature of the cellulose solution or the viscous liquid employed, it was necessary to coagulate the threads on the endless cloth, or to dry them by means of steam. This tulle could then be made waterproof, or receive other supplementary treatment. By varying the speed of the endless cloth and the to-and-fro movement of the capillary tube, it is possible to vary the character of the meshes.

In 1901 another patent was taken out by Joseph Mugnier, of Lyons, for the manufacture of artificial tulle. This consisted of the preparation of a special solution, to which the inventor added glycerine and other products, which augmented the viscosity of the solution and added to the flexibility and strength of the product. Still another idea is that due to Emile Duinat, in 1906, in his French Patent No. 368,398. The solution of cellulose is forced through a rectangular slot in which rise and fall one or more sets of grips in the form of teeth ; these teeth divide or interrupt the continuous flow

of the solution, and the latter consequently emerges in the form of fine bands or ribbons, or of thick threads, and thus produces a kind of artificial tulle.

Villeurbonne has patented a process that consists of running the cellulose solution into the bas-reliefs of an engraved cylinder, of coagulating this cellulose, and then of removing the artificial tulle thus formed.

The simplest idea, however, as well as the most practicable, for the manufacture of this artificial tulle is that invented by Marius Ratignier, Director of la Société H. Pervilhac et Cie, Lyons. The process of Ratignier-Pervilhac gives a continuous arrangement which enables one to manufacture indefinite lengths of this new product.

Fig. 107 illustrates the apparatus. The solution of cellulose in the correct degree of viscosity is in the tank A, and flows uniformly on to the engraved cylinder B, which rotates in the direction of the arrow.

Fig. 107

All the parts which form the design are thus filled with the solution, and a thin layer may also be deposited on the remaining or plain parts of the cylinder. This thin layer is removed by the knife or scraper C. A coagulating liquid is forced from the pipe D, and impinges against the cylinder in its full width ; the surplus liquid falls into the bath E, and thus serves to complete the coagulation, while the bath E is kept at a constant depth by means of the overflow pipe F. The coagulating liquid is caught as it emerges from the pipe F, and used again. The artificial silk product is removed from the cylinder by an endless cloth G, which travels in the direction indicated, and the tulle, lace, or the like is finally wound on to a suitable drum. A jet of water from the pipe H flows over the full width of the engraved cylinder, B, and thus removes the chemical substances, while the recesses in the cylinder are dried by a current of warm air from J. The process is thus
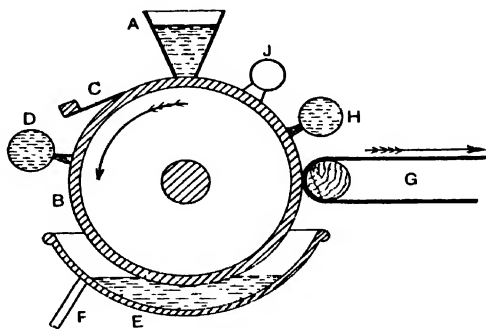
continuous, and any suitable design may be engraved on the metal cylinder.

Figs. 108 and 109 (Ratignier-Pervilhac) are photographical reproductions of artificial fabrics made by this process. The former is a kind of Madras muslin, while the latter is an artificial tulle. Fig. 110 is an enlarged view of the meshes in Fig. 109.

This interesting method did not stop at the experimental stage, for a great quantity of very beautiful artificial tulle has been made. At first sight it is difficult to distinguish it from ordinary tulle.
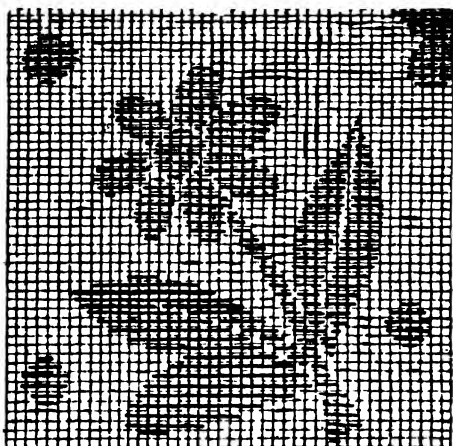
Fig. 108.

The artificial product is naturally less pliable than tulle made from ordinary textile threads, and it is also weaker; it has the lustre of artificial silk, and may be metallized or waterproofed. The product has been employed mostly for millinery purposes. It has been manufactured largely by La Cie française des Applications de la Cellulose, at Fresnoy-le-Grand, and is now manufactured in the United States of America by the inventors, Ratignier and Pervilhac, who make superb products.

La Cie française des Applications de la Cellulose has modified the original apparatus, and the modification is illustrated in Fig. 111. The network or meshes of artificial tulle are still formed on an engraved cylinder A, which rotates as indicated. The cylinder A is fitted accurately to, and immediately under, the rectangular tank B, which contains the solution of cellulose, and the latter is forced into the tank through pipe C by pressure. As the cylinder rotates, the engraved parts are filled with the solution, but the plain surface of the cylinder remains unaffected and clean. The cylinder A is hard in contact with the endless cloth D rotating as shown by the arrow E. The pressure

between the cylinder A and the cloth D causes the solution to leave the engraved parts and to adhere to the endless cloth. The cloth and contents pass into a suitable coagulating liquid in bath F. The artificial tulle thus formed is then detached from the endless cloth, passed over the roller G, and may then be wound on to perforated cylinders to be washed and dried. The advantage of this arrangement over that designed by Ratignier and Pervilhac is that the engraved cylinder is not required to enter the coagulating liquid.

In the Swiss Patent No. 57951 (1911), La Cie Applications de la Cellulose give a formula for a special solution of cellulose for the manufacture of artificial tulle. The method of preparation is as follows : 30 kgs. (66·12 lbs.) of cleaned and partially bleached cotton is pulverized in a suitable machine until all the fibres of cotton are reduced to powder. To this pulverized cotton is added a sufficient quantity of water to make up the total

Fig. 109.

volume of cotton and water to 3,000 litres (660 gals.). Then 60 kgs. (132·24 lbs.) of crystallized copper sulphate is dissolved in 300 to 400 litres (66 to 88 gals.) of water, and to this solution is added, little by little, 40 litres (8·8 gals.) of caustic soda. (The company indicates that this caustic soda lye, of 38° Bé., has been diluted by three to four times its volume of water.) The two solutions are then mixed, and the cellulose absorbs, almost immediately, all the hydroxide of copper. The surplus liquid is now removed by a
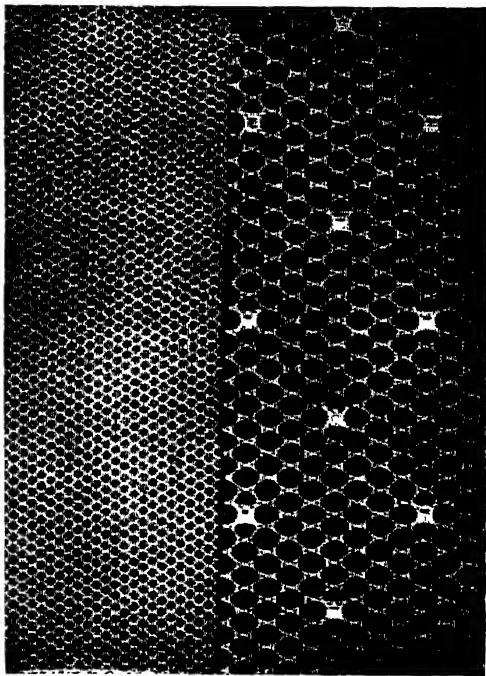
hydro-extractor, by pressure, or by filtration, and the residue of cellulose charged with hydroxide of copper is cut up into slices. The substance is then dissolved in 100 litres (22 gals.) of ammonia at 28° Bé. It is then left to work up for fifteen to twenty minutes and then allowed to stand for twenty-four hours. Finally, the mixer is restarted, and, with the object of completing the solution, about 0·6 litre (0·132 gal.) of caustic soda at 38° Bé. is added for each kilogramme (2·204 lb.) of dissolved cellulose. The preparation of this solution of cellulose is conducted at the ordinary temperature. It is obvious that this formula is not a simple one, and this probably
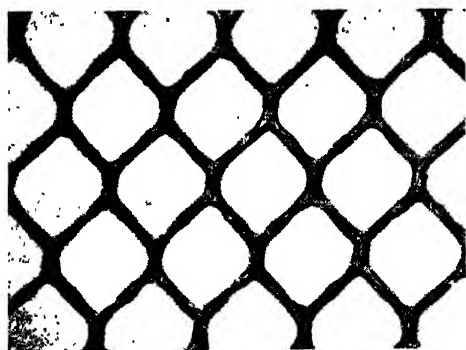
Fig. 110.

accounts for the fact that another process, much more practicable, has been introduced to achieve the same object.

In the British Patent No. 11714 (1911), la Cie des Applications de la Cellulose describes a process of coagulating artificial tulle in a caustic soda bath. When cellulose dissolved in ammoniacal copper oxide is precipitated in an acid bath, the acid removes almost immediately practically all the copper from the precipitated product, and leaves the substance nearly white ; whereas, if caustic soda or caustic potash is used for precipitation, the copper is only partially removed, and the product, thread or tulle, is blue. In order to remove the rest of the copper, it is necessary to pass the product through a dilute acid. Again, in employing alkalies for coagulation, the coagulating liquids themselves take on a deep blue colour in consequence of the presence of part of the copper which has been removed during the coagulation.

In the manufacture of artificial silk this deep colour formation is a disadvantage, for it prevents, to some extent, the operatives from seeing the thread clearly, and from controlling successfully the formation of the thread—a disadvantage which does not exist when coagulation is performed in acid baths. Such a disadvantage is increased in connection with the manufacture of artificial tulle, for it is necessary to see continually if the

tulle is properly made, and to make sure that no meshes remain in the engraved parts of the cylinder. The above French company has been able to prevent the deposition of copper in the liquid by adding to the alkaline coagulating bath 10 grms. of commercial white arsenious acid As_2O_3 per litre of caustic soda of 30 per cent., and keeping the mixture at a temperature of 60° to 65° C. (140° to 149° F.). The presence of the arsenious acid prevents the elimination of copper, and the soda bath remains clear and un-coloured, even after hav-ing been used for a month. On the other hand, the threads or tulle contain all the copper, and are therefore of an intense blue colour. The threads are wound on spools and the tulle on cylinders, then washed to remove the alkali, and finally the product is readily freed from copper in dilute H_2SO_4 at 5° Bé. without any precipitate of cupro-arsenious pro-ducts. The products obtained in this way

Fig. 111.

are, when dry, distinguished by their brilliancy, pliability and elasticity.
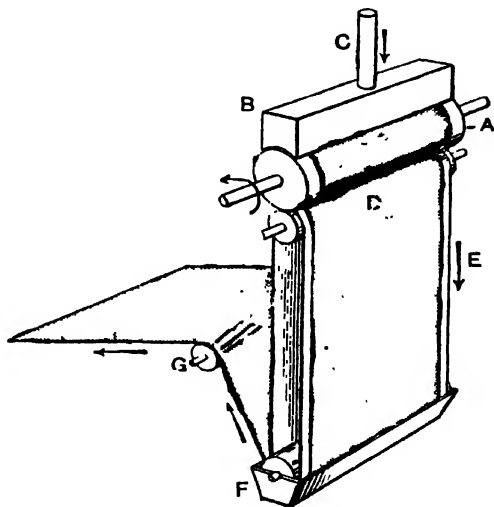
As we have already stated, the artificial tulle manufactured at Fresnoy-le-Grand has been used largely for millinery and the like, and, seeing that this artificial product is stiffer than natural tulle, it keeps its form better on the hats than does the natural article. The defective suppleness is therefore an important quality in artificial tulle, for natural tulle has to be starched or loaded with 3 grms. of starch per metre (40 grains per yard) in order to make it stiff and firm. Artificial tulle has not been used to any extent for other dress materials, because of its weakness.

The advantages of artificial tulle are—

(1) A low net cost.

(2) The employment of artificial tulle in comparison with natural tulle requires about 40 per cent. less material, because even light material remains stiff.

(3) The production is very quick, and in case of new fashions the delays in delivery are minimized on account of the ease with which a cylinder can be changed.

The selling price[1] of artificial tulle from La Cie des Applications de la Cellulose are as follows—

Plain tulle, 700 mm. wide (27¼ ins.), in all shades, is sold at 0·26 to 0·28 fcs. per metre (approx. 2¼d. to 2½d. per yard).

Metallic tulle (imitation of gold, silver, steel, etc.), 1·05 m. wide (39⁹⁄₁₆ ins.), at 0·80 fcs. per metre (approx. 7d. per yard).

Special tulle, at 1·10 fcs. per metre (approx. 9¾d. per yard).

Another process for the manufacture of artificial tulle and lace according to the U.S.A. patent is that by Joseph Foltzer (Swiss Patent No. 69,514, October, 1913) : Method of making artificial textile products from solutions of cellulose or plastic substances, nitro-cellulose, viscose, cellulose of acetyl, and the like ; casein, fibrin, maixin and the like ; or from rubber. These solutions or substances are applied as thin layers, corresponding to the thickness of the desired body, by means of a spreading apparatus which deposits the substance on to a cylinder, an endless cloth, or some such suitable receptacle. The substance applied to the cylinder is stemmed in front of an engraved pressure or goffering roll which is placed either close to or at a short distance from the laying-on or spreading apparatus. This roll, which is positively driven and which presses against the cylinder, stamps out the viscous mass in forms which coincide with the engraving on the goffering roll.

The work may be performed by either of the methods illustrated in Figs. 112 and 113. The solution of cellulose or viscous mass contained in the spreading apparatus A in Fig. 112 escapes on to the cylinder D as a layer which corresponds in thickness to the depth of the engraved parts in the goffering roll B. The rollers rotate as indicated, and two wings or blades E which connect the laying-on apparatus to the roll B prevent the substance from escaping at the sides. The solution is fed towards the grip of the roll B and the cylinder D, but cannot proceed farther as a body. The engraved parts on the roll B, representing the design for tulle or other textile texture, become filled with the solution in virtue of the pressure, and by this time the substance is

[1] Pre-war price.

partially set so that it may be conveyed farther upon the circumference of the cylinder D and immersed in a hardening liquid contained in the tank C. Soon after the formed fabric emerges from the bath C it is detached from the cylinder D by means of the rollers F. It is then guided by rollers G, H, J and K into and out of the three vats L, M and N, which contain suitable liquids for the further treatment of the product—say, for example, precipitation, acidification and cleansing. The finished fabric is finally wound upon a roller P.

It has been found in practice that the stamped or pressed-out
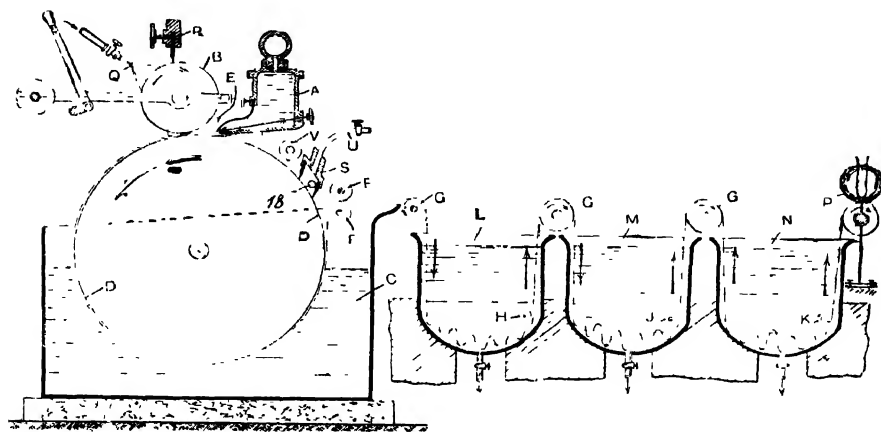
FIG. 112.

artificial products adhere very frequently to the engraved parts of the pressure roll D, from which they can be detached only with difficulty. This is particularly the case when thick embroidery is being made. To prevent this annoying feature, the roll B is sprayed with a liquid at Q which precipitates the solution, while the excess liquid is removed by the stripping knives R. The adhering of the substance to the engraved parts of the roller B might also be prevented by heating the roller to that temperature which causes a superficial coagulation. The outer surface of the cylinder D must also be cleaned very carefully between the rollers F and the outlet of the spreading apparatus A. Provided for this purpose are the receptacle S, the lateral outlet pipe 18, and the pipe U, through which may pass a cleansing liquid. As is indicated, the lateral walls of the receptacle S act as stripping

knives, while a heated drum V dries the surface of the cylinder D.

Special effects may be obtained if fine fibrous powder, either of one colour or of different colours, be mixed with the solution of cellulose, or if such powder be sprinkled on the roller B to enable it to adhere to the surface of the substance when the latter is stamped out. In order to impart a suitable surface to the products, liquid gum, tallow, fine metallic powder, and the like may be used.

The drying is effected in suitable drying machines provided with heated cylinders, and between flat or corrugated sheet metal, or between mountings for cards. The artificial products may also be dried in a centrifugal apparatus, or they may be wound up between two perforated sleeves, and then fixed to a shaft revolving with a high velocity. The centrifugal action prevents to a great extent the tendency which the products exhibit to contract during the drying process. This contraction takes place notwithstanding the tension which is exerted upon them ; hence, in choosing the dimensions of the various parts of the design, it has been found necessary to make the engraved parts of the roll at least 40 to 80 per cent. deeper and about 25 to 50 per cent. larger than the finished dimensions of the corresponding parts.

The raised parts of the finished product may be ornamented by passing the cloth between two goffering or silk-finishing calenders kept at the proper distance apart in order to preserve the maximum thickness of the fabric at these parts, and thus retain the contrast between the thin and the thick parts.

Instead of using a mass, say, of cellulose solution, one may use cotton fibres or protoplasm not completely dissolved by the solvent liquid, but only rendered soluble. There may also be mixed with the said mass, starch and gluten, dissolved, say, in lye, as well as a shining, homogeneously coloured glass powder (antimony). These dough-like substances help to make softer and less vitreous products, and the small particles of glass powder produce in the products special light effects. Instead of producing artificial metal-like bodies by adding metal powder to the mass, somewhat similar results may be obtained by a process of electroplating. Artificial products can also be metallized and covered with a layer of copper if iron powder is used and if the finished product is dipped into a solution of copper ; the presence of iron causes the

copper to precipitate in the form of a thin layer on the fabric—
the latter may then be covered with lac. Cheap artificial
textile goods have only to be covered with a metallic or glazed
lac. It is also possible to make light, soft and porous products
by preparing a mass consisting of two different solutions made
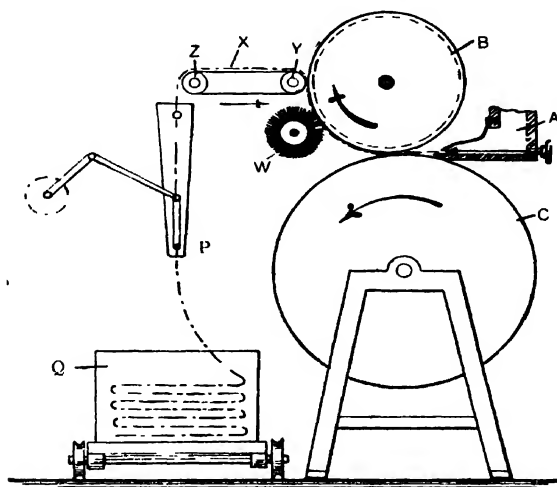from different raw materials—for example, a solution of

Fig. 113.

cellulose and of fibrin ; one of these (say, the fibrin) is after-
wards recovered or withdrawn. There remains then a con-
nected microscopic skeleton which can easily be coloured, and
which is particularly soft to the touch.

Another apparatus, by J. Foltzer, for the treatment of the
above-mentioned substance is illustrated in Fig. 113. The
spreading apparatus A delivers the solution on to the cylinder
C revolving in the direction shown. The substance is caught
between the pressure or goffering roller B as before, in order
to squeeze the substance into the engraved pattern. This
cylinder, as well as the similar one in Fig. 111, may be replaced
by a plate or by an endless band. The speed of the pressure
roller B may be quite independent of that of the cylinder
C ; in other words, the surface speed of one may be greater
or less than that of the other. If there is a difference in the
surface speeds it is evident that a certain amount of friction
will obtain where the two meet, and this results in improved

stamped-out products. If there is a small gap between the roller B and the cylinder C, the resulting product will consist of the same design on a film-like base, the thickness of which base corresponds to the gap. This arrangement enables one to produce plastic incrustated transparent films.

It is a common practice to make the pressure rollers in segments instead of one solid roller, and particularly when it is desired to insert vertical stripes in the patterns. The same type of stripe may be wanted in different positions for two distinct orders, and it is clear that the above arrangement permits of any particular stripe section being changed to the proper position for the second order by sliding the section on the shaft and re-arranging the other sections.

For the manufacture of products that have to be perforated, the pressure roller B may be provided with a stripping brush W, which brushes off and removes the thin film parts which cover the gaps between the required design. In this machine it will be noticed that the product touches the cylinder C only at the nip, and then is carried forward and upwards towards the travelling cloth X on rollers Y and Z. From the latter position the cloth drops off the travelling cloth into the plaiting-down apparatus P, and ultimately into the barrow or wagon Q. The loosely folded product in this barrow is then successively acted upon by different baths and chemical solutions which may precipitate, treat, cleanse, and ultimately bleach or dye the fabric. This method minimizes the handling of the delicate textures and also minimizes the damages.

The cleansed products may be treated with magnesium chloride, glycerine, or glycerine-like solutions, and they may then be wound up between wet cloth bands while a slight tension is being imparted to them. In this state the products are dried. In order to obtain the necessary tension, the products may, if desired, be dried on fine needle-fields or rollers covered with fine card clothing.

These textile products are defective in that their thicker parts feel much harder than the similar parts of ordinary textiles or embroidery. On the other hand, it is possible to effect an improvement in an indirect manner. Since the engravings of the pressure roller have to be 50 per cent. to 80 per cent. deeper, and also larger, than the corresponding parts of the finished dried product, much softer and more plastic thick threads are produced, not by a continuous deep

engraving as at Y in Figs. 114 and 115, but by engravings with interrupted parts as illustrated in Figs. 116 and 117. In Fig. 116 the parts Y represent the clean cut-out and deep parts of the engraving, while Z shows a series of vertical ribs in the remaining parts. After the fabric is dried, the breaks formed by the ribs are scarcely visible ; they form, however, a kind of joint which makes the product much more flexible.

We may state that there is the prospect of a new industry being established in which by means of a series of technical
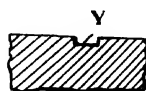
FIG. 114. FIG. 115.

and chemical operations, light cotton muslins will be transformed into transparent tissues of a silk-like character. In order to effect this transformation, the fabrics pass through several acid and alkaline baths, which preserve the solid
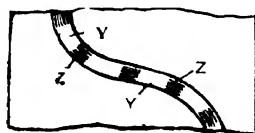
FIG. 116. FIG. 117.

character of the cloth and yet enable the fabrics to be washed like ordinary cotton fabrics. They have a beautiful lustre, which, however, is not so marked as that in artificial silk fabrics. The process has the advantage of preserving in the transformed fabric all the strength of the original fabric, and at the same time of·imparting a silky and transparent effect at a comparatively low cost—a few pence per square yard of cloth treated. One machine can produce from 1500 to 2000 metres (1,640 yds. to 2178 yds.) of transformed cloth per day. It is quite possible that this process will compete with the artificial silk processes in many cases.

In the second English edition of this work, it was stated that many persons had fears of overproduction of artificial silk, because of the many new firms that were being established, and the increasing additions to existing firms. It was also stated that in spite of the great advances made in the artificial silk industry, there would appear to be even more room for expansion, for this industry is still a small one when compared with some of the other textile industries. This opinion was justified even before the third edition went to press, for great extensions were contemplated and some of them effected ; further extensions have taken place since the publication of the third edition of this work in January, 1926. It is estimated that in the undermentioned four groups, the world's production in 1923 was—

Cotton	.	.	.	.	.	11,200,000,000 lbs.
Wool	.	.	.	.	.	2,912,000,000 ,,
Natural silk	.	.	.	.		76,000,000 ,,
Artificial silk	.	.	.	.		98,560,000 ,,

Consequently, the amount of artificial silk, great as it is, represents less than 1 per cent. of the production of cotton, and even if the production of artificial silk is doubled in two or three years, there seems little fear of overproduction. Even if the price of the manufactured product is lowered, it is quite possible that this will be compensated for partially, if not wholly, by simplified and improved methods of manufacture, perhaps jointly by reduction in labour, prevention of excessive waste, and more perfect methods of recovering by-products.

APPENDIX

WITHIN recent years there has been a considerable amount of attention paid to the development of various kinds of artificial silk and to the use of the different products in the textile industry. The firms in each group that manufacture yarns according to the different processes vie with each other in their efforts to produce improved qualities and newer types of yarn and to place the same in the world's markets. The same compliment should be paid to all those who are engaged in the handling of these yarns in the subsequent industries of weaving, knitting, dyeing and finishing. All recognize that a minimum amount of handling of the various goods is bound to be reflected in an improvement in the finished product, and hence methods that were common in some of the industries are being replaced by more suitable methods of handling the delicate products. This phase is really apparent in practically all branches. In some cases the changes made are simple, but in other cases more or less automatic and semi-automatic mechanism have been devised to handle the material with the least possible friction, and to secure uniformity in all directions. The greatest development is probably found in those industries where the newly-formed yarn has to be treated with some kind of liquid, e.g. bleaching, dyeing, washing, drying, and the like.

Originally, one of the greatest assets of artificial silk yarn was its lustre. For many purposes a highly lustrous yarn is of very great value, but for other purposes a more subdued effect is desired. In those cases where the lustre was unsatisfactory or undesirable, a method of reducing the lustre or dimming the lustre has been resorted to. Again, the density of the yarns was considered a drawback in some respects, and hence there has appeared on the market a hollow fibre that supplants the solid one in the manufacture of particular types of garments. The same area in a cloth or garment can obviously be covered with less weight of yarn by means of hollow fibres than is possible with solid fibres of the same diameter. Each filament in the yarn is a tube. This so-called covering action is indeed more pronounced than what would appear at first

sight possible, because the threads compounded of hollow filaments have a tendency to collapse, and thus the space is more effectively covered.

Continuous lengths of various kinds of artificial silk are now cut up into well-defined lengths, say from 6 in. to 12 in., so that they may be mixed or blended with fibrous material such as wool and cotton. The percentage composition may, within limits, be as desired, and many yarns are made in which the fibrous material is mixed with the short lengths of artificial silk in about equal proportions. As a rule, however, the fibrous material, and particularly wool, predominates in the mixture. Since the continuous lengths of artificial silk are cut into comparatively short lengths of a few inches the resulting product is termed " staple fibre," and occasionally termed " artificial wool." Its chief use in such mixtures, and especially when blended with wool, is to impart lustre—the wool supplying its usual property of warmth. As a matter of fact, these new combinations have opened up a new field by producing a novel form of union textures. Incidentally, it has made the work of the dyer and finisher more difficult.

The bulk of artificial silk yarns is still absorbed by the knitting industry, but a gradually increasing amount is finding its way into other industries. A certain amount of caution has to be exercised when an attempt is made to introduce an absolutely new type of yarn such as artificial silk, and it is only natural to expect that the first attempts would be made to introduce the yarn as weft in the weaving industry, and this for two very important reasons—

1. Because it is so easy to introduce weft, as the experimental quantity can be as small as desired : the tension on the yarn is comparatively slight ; and a variety of colours can be used with a minimum of expense.

2. Because, with few slight alterations, the existing looms can be utilized for the weaving of artificial silk weft.

And this particular type of combination, i.e. artificial weft in conjunction with warp yarns made from cotton, wool, worsted, linen and real silk, forms a considerable part of the new industry. It must not be forgotten, however, that much care has to be exercised to secure uniformity in the tension of the weft, in order to prevent " bright " picks, and in the elimination or partial elimination of friction.

The introduction of a few threads of artificial silk in the

warp to produce stripe effects of various colours and widths involves much more care for various reasons. Thus, the extra tension necessary, and the increased amount of friction—compared with weft—means many more breakages, both in the threads and in the constituent filaments. Again, in regard to the production of a given length of cloth, the variation in the length of the artificial silk threads as compared with the length of the other threads in the warp, due to different weaves and to different degrees of take-up and shrinkage in subsequent operations, has to be considered very carefully, otherwise faulty cloth will result. This type of combination is also largely adopted, and will probably increase as more experience is gained with the behaviour of the various kinds of threads during the weaving and finishing operations.

Artificial silk waste is also used in combination with higher qualities of the same material, as well as with fibrous materials to form mixture yarns and fabrics.

Attempts have been made, with a certain degree of success, to produce artificial silk yarns that resemble wool yarns. There may be a great resemblance in the look of the wool yarn and its copy, but it seems unreasonable to expect yarns made from vegetable matter to possess the same properties as yarns made from animal matter. Nevertheless, the artificial silk product can be successfully blended, as it is possible to card, comb, and spin the imitation fibre in combination with wool fibres.

As already indicated, there are difficulties to be met in the weaving of artificial silk warps, but, in virtue of the great improvement in the yarns, both in strength and suppleness, it is now possible to manufacture fabrics composed wholly of artificial silk yarns. Moreover, since it is a common practice to use two or more kinds of yarns, that is, of different composition, it is possible to multiply the effects when the resulting fabrics are dyed and finished.

The introduction of various kinds of artificial silk yarns into the latter class of fabrics, or as a component part of such a range of yarns and fabrics as those mentioned, has obviously increased the difficulties of the dyer and the colour maker. These difficulties have been further aggravated by the fact that there are at least four different kinds of artificial silk (see page 21), and some of these behave quite differently from the others when immersed in certain dye liquors.

None but those who are intimately connected with the production and use of dyestuffs have any conception of the troublous times that have confronted the colour maker and the dyer since the introduction of artificial silk yarns.   There were plenty of difficulties before the advent of these artificial yarns, but they have been multiplied in proportion to the various kinds of yarn invented and to their use in union fabrics. ₜIn the first place, the very nature of the material, and especially in yarn form, necessitates the elimination of practically all methods of handling such as were common in certain dyehouses not many years ago.   It is quite true that much complex mechanism has been employed for decades in the dyeing industry, but the use of such mechanism, involving various kinds of motion that were not used before the advent of artificial silk yarn, is now much more common than heretofore. Moreover, modifications in the methods of dyeing have been found necessary in order that uniformity of shade or tint may result.   Some little instruction in relation to the dyeing of artificial silk will be found on pages 221 to 223, but it need hardly be said that a modern book on dyeing should be consulted for detailed information.

Nothing but experience and the use of a fast and effective dye will suffice in garment dyeing, because it is difficult for the dyer to ascertain exactly the nature and constitution of the yarns that were used in the manufacture of the cloth from which the garment was made.   Thus, there may be two or more varieties of artificial silk in addition to a similar number ₜof ordinary fibrous yarns.   More uniform effects can be expected when only one variety of artificial silk is used, although care has to be exercised in the yarn department and in the weaving department to avoid mixing of various pirns or quills. When there is no distinction made between the empty pirns and quills that are used for holding the weft yarn, it is difficult• to avoid mistakes.   In this respect, it would probably be a wise plan if the various groups of artificial silk manufacturers could come to some agreement regarding the standardization of their pirns, bobbins, quills, and•the like, so that viscose, nitrocellulose, cuprammonium and acetate silks could be distinguished at once by the colour, shape, or other suitable features of the foundation of the package.

Great developments have taken place in the manufacture of dyestuffs suitable for dyeing artificial silk.   The following

information is included by permission of Messrs. British Dye-stuffs Corporation, Limited, Manchester.

IDENTIFICATION OF ARTIFICIAL SILKS

The following are a few simple tests for distinguishing between the principal types of artificial silk on the market.

I. *Solution of iodine in potassium iodide*

Viscose	—Greenish-blue
Cuprammonium	—Bluish-green
Nitro	—Reddish-blue
Acetate	– Reddish-brown

II. *Tests for distinguishing between Acetate and other Artificial Silks*

Acetate silk burns in a similar manner to natural silk, leaving a cinder, whilst the other artificial silks burn like cotton, leaving only a fine white ash.

Acetate silk is readily soluble in acetone, whilst the other artificial silks are unaffected by this solvent

III. *Test for distinguishing between " Lustron " and " Celanese " Acetate Silks*

Lustron is soluble in chloroform.

Celanese forms a jelly with chloroform, but does not completely dissolve.

IV. *Test for distinguishing between Viscose and Cuprammonium Silks*

Ammoniacal silver nitrate solution.

Viscose	—Reddish-brown
Cuprammonium	—Practically unstained

V. *Test for Nitro Artificial Silk*

This silk becomes blue when immersed in concentrated sulphuric acid containing a few crystals of diphenylamine.

THE DYEING OF ARTIFICIAL SILKS

Before dealing with the actual dyeing operations, it is necessary to describe some of the peculiarities associated with these fibres.

These are almost entirely connected with the method of manufacture of the yarn, which consists of the twisting together of a

number of endless filaments immediately after their formation. The formation of the filaments and the twisting into yarn being one continuous operation, there is no opportunity of mixing the filaments from several spinning operations to make one thread, so that the blending of different qualities of materials normally associated with the spinning of all natural fibres is lacking.

It is quite probable that the differences, partly chemical and partly physical, between two lots of yarn spun at different times are no greater than the differences between two samples of wool, cotton, or even natural silk, but the lack of blending facilities prevents the application of the usual means of minimizing these irregularities, with the result that it is not uncommon to find two or even three different shades in one batch of dyed yarn.

According to Clement, in the *Färber Zeitung*, " All the artificial silks possess the defect, when dyed in bulk or in cloth, of giving stripes of different intensities of shade. In the case of collodion silks, i.e. the Chardonnet type, this defect has been traced to differences in the percentage of residual nitrogen remaining after denitration, the darker shades corresponding to the higher percentage of nitrogen. In the case of Glanzstoff, i e. cuprammonium silk and viscose silk, the darker stripes correspond with a more pronounced oxy-cellulose reaction."

H. Dahlenvord (*Textilberichte*, 1925 ; 6, 823) ascribes this uneven dyeing to variations in the structure of the fibre due to different velocities of coagulation during the spinning process; to xanthogenation at too high a temperature and to incomplete mercerization of the raw cellulose.

This problem of lack of uniformity and consequent uneven dyeing is receiving the very closest attention of the makers of all kinds of artificial silks, and though a steady improvement is being made the problem is still a long way from being completely solved.

In the meantime, a great deal can be accomplished by a correct choice of dyestuffs, some of which are found to be much less affected than others by the lack of uniformity in the artificial silk.

A property peculiar to artificial silks is their lack of tensile strength, particularly when wet. This property renders careful handling very essential, and prohibits the dyeing of warps in the chain.

Probably associated with this is the tendency to swell and to become somewhat plastic, which renders the dyeing of yarns in the cheese an impossibility. For the same reason, wet yarn or material should not be wrung out or pressed through squeezing rollers, but should in all cases be hydro-extracted to remove excess of water.

DYEING PROCESSES

Nitro, Cuprammonium and Viscose Silks

As all these artificial silks belong to the regenerated cellulose groups, it is not necessary to differentiate between them. They may all be dyed with the classes of dyestuffs suitable for cotton, namely, direct cotton colours, basic colours on a mordant, sulphur colours or vat colours.

Yarn is dyed in the hank, and is turned by hand or by machine. In either case it must be handled carefully, on the one hand to avoid broken filaments and on the other hand to avoid the slipping of the leases, both of which give rise to serious loss in the subsequent winding operation. It has been found that by dyeing with much less of the hank immersed in the dye-liquor than is usual with other materials, a great deal of the lease difficulty may be obviated.

Pieces are dyed on a winch so constructed as to put as little strain as possible on the material. Any inequality in the original artificial silk shows itself in the form of bars of paler or darker hues, but it must not be assumed that bars arise solely from this one cause. Undue tension when the fibre is being knitted, or even undue tension during dyeing, will bring about similar results.

DIRECT COTTON COLOURS

The direct cotton colours may be dyed in the same way as on cotton ; soluble oil added to the dyebath helps levelling and gives a soft handle. The amount of dye-liquor used should be from 20 to 30 times the weight of the material, that is 2 to 3 gallons for each pound of the goods.

As in cotton dyeing, for full shades and blacks a short dye-liquor should be used.

For light shades dye at from 90°–120° F. (32°–50° C.), with an addition of 1 per cent soda and soluble oil to the dyebath.

For light to medium shades. dye at 120°–150° F. (50°–65° C.), with an addition of 1–1½ per cent. soda, and 5–10 per cent. Glauber's salt, with or without the addition of soluble oil.

For medium to dark shades dye with 1–2 per cent. soda, 20–30 per cent. Glauber's salt calc., or common salt ; the dyeing temperature may be from 150°–190° F. (65°–88° C.), or even at the boil if the material is carefully handled.

In the case of medium to dark shades, standing baths may be kept, replenishing the dyebath for succeeding lots with from one-half to three-quarters the original amount of dye.

The methods of after treatment with metallic salts, formaldehyde, or diazotizing and developing, such as are used for cotton, may also be used for these artificial silks, though it must be remembered that

prolonged handling in the wet state undoubtedly has a deleterious action upon them.

The nitro silks have a somewhat less affinity for direct cotton colours than the cuprammonium or viscose silks.

Direct colours suitable for these artificial silks are—

Yellows—
Chlorazol Yellow 6G
Chlorazol Fast Yellow 5GK
Chlorazol Fast Yellow B
Chrysophenine G
Titan Yellow G

Oranges—
Chlorazol Fast Orange G
Chlorazol Fast Orange R
Toluylene Orange R
Chlorazol Orange RN

Reds —
Benzopurpurine 4B
Benzopurpurine 10B
Chlorazol Fast Eosine B
Chlorazol Fast Scarlet 4BS
Chlorazol Fast Red K
Chlorazol Fast Red FG 9202K
Congo Rubine
Chlorazol Fast Bordeaux LK
Chlorazol Pink Y
Titan Scarlet CB
Congo Red W. Conc.
Chlorazol Fast Rubine LF

Violets—
Chlorazol Violet N
Chlorazol Fast Helio BK
Chlorazol Violet WBX
Chlorazol Violet R

Blues—
Chlorazol Blue B
Chlorazol Blue 3B
Chlorazol Blue RW
Chlorazol Fast Blue 2B
Chlorazol Sky Blue FF
Chlorazol Sky Blue GW
Chlorazol Black BH
Chlorazol Diazo Blue 2B

Greens—
Chlorazol Dark Green PL
Chlorazol Green BN
Also, combinations of the previously mentioned yellows and blues.

Browns —
Chlorazol Orange Brown X
Chlorazol Brown G
Chlorazol Brown B
Chlorazol Fast Brown RK
Chlorazol Brown M
Chlorazol Drab RH
Chlorazol Brown LF
Chlorazol Brown 2G

Greys and Blacks—
Chlorazol Fast Black BK
Chlorazol Black SD
Chlorazol Black E Extra
Chlorazol Black LF
Chlorazol Black GF

NOTE.— Any dyeings produced from the foregoing list may be brightened by topping with basic colours dyed in a fresh bath made acid with acetic acid and dyed cold.

These colours give all-round good results, but, as previously mentioned, certain dyes cover up inequalities in the silk better than others, and the best of these are given in the following lists—

EVEN SHADES

Yellows—
Chlorazol Yellow 6G
Chrysophenine G
Chlorazol Fast Yellow 5GK
Titan Yellow 2G

FAIRLY EVEN SHADES

Chlorazol Fast Yellow B

Even Shades	Fairly Even Shades
Oranges—	
Chlorazol Fast Orange G	Chlorazol Fast Orange R
	Toluylene Orange R
	Chlorazol Orange RN
Reds—	
Chlorazol Fast Red K	Congo Red W. Conc.
Chlorazol Fast Red FG 9202K	Congo Rubine
Chlorazol Fast Bordeaux LK	
Chlorazol Fast Rubine LF	
Chlorazol Pink Y	
Titan Scarlet CB	
Violets—	
Chlorazol Fast Helio BK	Chlorazol Violet R
Chlorazol Violet WBX	
Blues and Greens—	
Chlorazol Diazo Blue 2B	Chlorazol Dark Green PL
(Direct and Developed)	
Browns—	
Chlorazol Brown G	Chlorazol Orange Brown X
	Chlorazol Brown M
Blacks—	
Chlorazol Black SD	
Chlorazol Fast Black BK	

It is interesting to note that many of these direct cotton colours, when dyed with a trace of acetic acid in the dyebath, give more level results on uneven artificial silk than when the more usual method of dyeing in a slightly alkaline dyebath is employed. This latter method, however, needs less careful supervision.

BASIC COLOURS

All the basic dyes are suitable for the dyeing of nitro, cuprate, or viscose silks.

It is a common practice to dye basic colours, particularly in pale shades, without any mordant. Dyeing is commenced cold with the addition of 5–10 per cent. acetic acid, and the solution of the basic dyestuff is added in several portions. The temperature is then slowly raised to about 150° F. (65° C.).

These colours dye unmordanted viscose very evenly, but the fastness of such dyeings, both to light and washing, is inferior to that produced on a tannin-antimony or katanol mordant ; for the production of full shades a mordant is necessary.

Deep shades must be dyed on a mordant either of tannic acid or of the synthetic katanol, for which is claimed the property of covering inequalities in the artificial silk better than tannic acid.

Tannic Acid Mordant. The yarn is worked for a short time in a

bath containing 2–4 per cent. tannic acid and 0·5 to 1 per cent. hydrochloric acid at a temperature of 120–140° F. (50–60° C.). The material is then immersed for 2–3 hours, after which it is given a few turns, hydro-extracted and worked for 20 minutes in a cold bath containing 1–2 per cent. tartar emetic.

Katanol Mordant. The mordanting bath is made up as follows :

FOR 100 LB. VISCOSE

6 lb. katanol are dissolved with the addition of
4 lb. soda ash and the liquor made up to
120 gallons, to which is added
50 lb. common salt.

The goods are then treated for 2 hours in the mordanting bath at a temperature of 120–140° F. (50–60° C.), when they are removed and rinsed.

For light to medium shades, use 3–4 lb. katanol, 1½–2 lb. soda ash, and 25 lb. common salt.

Dyeing is carried out as described above.

All basic colours are suitable for dyeing these artificial silks, the principal ones being—

Yellows—

    Acronol Yellow T
    Auramine O

Reds—

    Magenta Crystals
    Safranine T. Conc.
    Tannin Pink C.

Blues—

    Victoria Blue B
    Turquoise Blue G
    Methylene Blues

Violets

    Methyl Violet 2B
    Methyl Violet 10BL

Greens—

    Brilliant Green Crystals Y
    Malachite Green Crystals A. Conc.

The following colours are the most even dyeing of this series (tannin-antimony or katanol mordant)—

Acronol Yellow T
Auramine O
Acridine Orange RS

Bismarck Brown R 100s
Methyl Violet 2B
Methyl Violet 10B

SULPHUR COLOURS

Sulphur colours are not extensively dyed on these artificial silks, possibly because matching to shade is rather difficult and the dyeing process may, therefore, be prolonged with a subsequent high loss in the winding operation and also possibly because of the fact that they give uneven shades on varying qualities of silk. Speaking of these colours as a class, they possess very good fastness to light, washing and cross-dyeing, and cannot, therefore, be too lightly dismissed.

The sulphur colour is dissolved by boiling with the concentrated solution of an equal weight of sodium sulphide concentrated and about 5 per cent. soda ash calculated on the weight of the artificial silk.

This solution and 5–30 per cent. Glauber's salt, calculated on the weight of the silk, are added to the dyebath and the temperature raised to 140° F. (60° C.). The addition of a little turkey red oil is also an advantage.

The wetted out yarn is entered and worked in the cooling bath for ¾ hour. It is then taken stick by stick, and after the excess dye-liquor has been roughly squeezed out by drawing through two dye sticks placed one on each side of the yarn, it is given a turn in a fresh bath of cold water containing a little sodium sulphide. After two further rinsing waters, the yarn is hydro-extracted and dried.

All the sulphur colours are suitable, the principal ones being—

Thionol Yellow Y	Thionol Brilliant Green G. Conc.
Thionol Yellow GR	Thionol Khaki WH
Thionol Yellow R	Thionol Brown B
Thionol Orange R	Thionol Brown O
Thionol Corinth RBX	Thionol Brown P
Thionol Corinth 2R	Thionol Brown GRR
Thionol Purple B. Conc.	Thionol Black Brown G
Thionol Blue 2BN	Thionol Black XXN Conc.
Thionol Navy Blue R	Thionol Black OG
Thionol Direct Blue S	Thionol Black 6R
Thionol Sky Blue PX	Liquid Sulphur Black L
Thionol Green B	Liquid Sulphur Black R

NOTES

Thionol Sky Blue PX and Thionol Brilliant Green G Conc. must not be dyed at temperatures higher than 120° F. (50° C.).

Thionol Green B and Thionol Black XXN Conc. become considerably brighter by an after-treatment with hydrogen peroxide.

The sulphur colours on artificial silk can be after-treated with copper-bichrome in order to increase their fastness to light and washing in the same manner as when dyed on cotton.

VAT COLOURS

These colours are finding an increased and extended use on viscose, in view of the present-day demand for increased fastness. Dyestuffs of the Duranthrene (anthraquinone) series satisfy the highest demands for guaranteed goods from the points of view of fastness to light and washing, and in most cases to chlorine. Their general fastness to acids, alkalis, and cross dyeing is also of the highest degree.

Individual members of the Durindone (indigoid) class possess excellent fastness to chlorine and to cross dyeing and find use on that account

Even Dyeing

With respect to even dyeing, there is a marked difference between the Durindone and the Duranthrene vat colours   The former, as a class, are satisfactory while the latter, with a few exceptions, are noticeably inferior.

The following colours dye evenly viscose silk of varying quality—

Durindone Red B, 3B, Y	Duranthrene Red BN
Durindone Blue 4B, 5B, 6B	Duranthrene Red Violet 2RN
Duranthrene Red 5G	Duranthrene Brown B

Dyeing Processes

The processes for applying these colours on viscose require several slight modifications in comparison with those used for cotton.   Whilst the general principle, that of reduction with sodium hydrosulphite and solution of the leuco body in caustic soda, remains the same, the affinity of the bulk of the vat colours for the viscose fibre is so very great that means have to be found to reduce that affinity to a degree where the best possible results as regards level dyeing are obtainable.   This can be brought about by the following methods—

(1) An increase in the ratio of liquor to material.

(2) A reduction in the amount of caustic soda in the bath.

(3) The addition of soap to the dyebath.

(4) In certain cases, a readjustment of the dyeing temperature.

(5) The use of retarding agents, such as fish glue, etc.

While on cotton, B.D.C. vat colours are divided for dyeing, purposes into two groups, namely, hot dyeing and cold dyeing colours, with viscose, on the other hand, an all-round dyeing temperature of 110–120° F. (40–50° C.) is best employed.

' These colours must not be applied in vessels containing copper fittings, but monel metal or similar nickel alloys are not injurious.

Duranthrene Colours

Process No. 1a. For Duranthrene Yellow G. Extra, Duranthrene Golden Orange Y, Duranthrene Golden Orange 2RT, Duranthrene Blues 3GT, GCD, CC, and RD Extra, Duranthrene Brown B, Duranthrene Claret B.8720, Duranthrene Dark Blue BO and Duranthrene Violet 2R—

30 lb. yarn in 120 gallons dye-liquor at 110–120° F. (40–50° C.)

Dyestuff Paste	Caustic Soda 76° Tw.	Hydrosulphite powder
1 lb.	2½ pints	1½ lb.
3 lb.	3½ pints	1¾ lb.
6 lb.	5 pints	2 lb.
10 lb	6 pints	2½ lb.

and 1–1½ lb. soap (dissolved). In pale shades, 1–1½ lb. fish glue can also be added.

Duranthrene Olive GL, which is supplied in powder form only, is dyed in the same way as paste colours above, except that one quarter the amount of dyestuff powder as of paste is taken, the amounts of caustic soda and hydrosulphite remaining the same.

Process No. 2a. For Duranthrene Red 5G, Duranthrene Red BN Duranthrene Red Violet 2RN, Duranthrene Olive R, and Duranthrene Brilliant Violet R.

30 lb. yarn in 120 gallons dye-liquor at 110° F. (40° C.).

Dyestuff Paste	Caustic Soda 76° Tw.	Hydrosulphite Powder
1 lb.	2½ pints	1½ lb.
3 lb.	3½ pints	1¾ lb.
5 lb.	4 pints	2 lb.
10 lb.	5 pints	2½ lb.

and 1–1½ lb. soap (dissolved) and in pale shades, ¾–1 lb. fish glue can be added.

Dissolving the Dyestuff

Soft water should be used for the dissolving and dyeing of these colours. If this is unobtainable, it is advisable to add 1 lb. soda ash per 100 gallons water.

The dyebath is filled with water, the caustic soda (and soda ash, if necessary) added and the temperature raised to 110–120° F. (40–50° C.). Any lime salts which rise to the surface are skimmed off and the hydrosulphite powder stirred in. The dyestuff (previously made into a thin paste with warm water) is added through a fine sieve to the dyebath, stirring gently for 15–20 minutes when complete solution should have taken place. Then the dissolved soap or fish glue is added.

DYEING

The yarn is dyed in the customary manner, but must be very smartly turned on first entering, to avoid any tendency towards " ending." The actual dyeing process should be completed in 20–30 minutes. As an alternative, the colour, in solution, can be added in two or three portions.

The yarn, on being removed is immediately rinsed in cold water, and oxidized by exposure to the air, or by giving it a few turns in cold ½° Tw. hypochlorite of soda solution, then soured off and washed well. Hypochlorite of soda should not be used in those cases where the colours are not fast to chlorine. Afterwards the yarn is given three or four turns in a soap solution, using 1½–2 lb. soap in 120 gallons at a temperature of 180–200° F. (83–93° C.), and rinsed well in warm water to clean off soap.

Durindone Colours

Process No. 3a.   For Durindone Red Y, B, and 3B, Durindone Blue 4B, 5B, and 6B.

For 30 lb. yarn in 120 gallons at 120° F. (50° C.)

Colour Paste	Caustic Soda 76° Tw.	Hydrosulphite Powder
1 lb.	2½ pints	1 lb.
3 lb.	3¾ pints	2 lb.
6 lb.	4 pints	3 lb.
10 lb.	5 pints	4 lb.

and 1-1½ lb. soap (dissolved). For pale shades an addition of 1–1½ lb. fish glue may be made.

The equivalent amounts of the powders are treated as in Process 1a. The Durindone Reds and Durindone Blue 4B are reduced in the so-called " stock vats " at 140° F. (60° C.), using about 2 gallons water to 1 lb. paste, with the requisite quantities of caustic soda and hydrosulphite powder and a small amount of soluble oil.

The Durindone Blues 5B and 6B should be reduced in the ordinary way in the bath, along with ¾–1¼ pints soluble oil to aid solution.

The dyeing is carried out as given under Process 1a. The Durindone Reds can be oxidized with sodium hypochlorite solution. Durindone Red B is not very fast to soaping, and it is preferable to dispense with this process. Durindone Red Y and Red 3B can be soaped in the ordinary way.

The Durindone Blues should be washed off, allowed to oxidize in the air, and then soaped as usual.

The following is a list of suitable vat colours for dyeing viscose—

Duranthrene Yellow G Extra Paste
Duranthrene Golden Orange Y Paste
Duranthrene Golden Orange 2RT
Duranthrene Olive GL Powder
Duranthrene Olive R Paste
Durindone Red B Paste –3B Paste Y Paste
Duranthrene Red BN Paste
Duranthrene Claret B 8720 Paste
Duranthrene Red Violet 2RN Paste

Duranthrene Brilliant Violet R Paste
Duranthrene Violet 2R Paste
Durindone Blue 4B Paste—-5B Paste –6B Paste
Duranthrene Blue 3GT Paste
Duranthrene Blue CC Paste
Duranthrene Blue GCD Paste
Duranthrene Blue RD Extra Paste
Duranthrene Dark Blue BO Paste
Duranthrene Brown B

DYEING CELLULOSE-ACETATE SILK

" Celanese " (British Celanese, Ltd.).
" Rhodiaseta " (Usines de Rhone).
" Lustron " (Lustron Co.).

Cellulose-acetate artificial silks are dyed with special dyestuffs, viz. : the " Duranol " colours and the " Ionamine " colours together with a few " Cellutyl " colours.

The Duranol colours are characterized by their excellent fastness properties and simplicity of dyeing, whilst the Ionamine colours possess very good affinity for acetate silk and give bright shades

many of which are capable of being diazotized and developed on the fibre. Ionamine A, diazotized and developed with beta-oxy-naphthoic acid, is the standard black for cellulose-acetate silk.

DURANOL COLOURS

Duranol Orange G Paste
Duranol Red G Paste
Duranol Red 2B Paste

Duranol Violet 2R Paste
Duranol Blue G Paste

These are direct dyeing colouring matters in paste form which are applied in the simplest possible manner, and require no after-treatment. Although insoluble in water, they dye easily level and are of very good all-round fastness. In fastness to light especially they are greatly above the average, while their fastness to washing and rubbing and freedom from sublimation are such as to meet far reaching requirements.

DISPERSOL COLOURS

Dispersol Yellow 3G Paste

This is a direct dyeing bright greenish yellow colouring matter in paste form which is applied in the same manner as the Duranol colours. Its fastness to light is sufficient for most normal requirements, but it is not in this respect quite equal to the high average of the Duranol colours, and, therefore, is not included in that range. Otherwise, it is of very good or excellent fastness and is especially distinguished from many other colours of yellow shade by its non-phototropic* properties.

IONAMINE COLOURS

This series of dyestuffs is distinguished from the duranols by being soluble in water. Their fastness properties in general are very satisfactory, and although they do not show the same high resistance to light as do the latter, they will satisfy the majority of requirements in this respect. Some members of the series are of interest as regards their direct shades only, others as regards the shades obtained by diazotization and development on the fibre, others for both their direct and developed shades.

The range comprises the following—

For direct dyeings only :

Ionamine Red KA

Ionamine Orange CB

For direct and also for diazotized and developed dyeings :

Ionamine MA
Ionamine B

Ionamine GA

NOTE. Ionamine MA in direct (yellow) shades is somewhat phototropic.

* A phototropic colour is one that fades or changes in shade on exposure to daylight, but regains its original colour on remaining for some time in the dark.

For diazotized and developed dyeings only :
> Ionamine H
> Ionamine L Paste
> Ionamine A

The duranol, dispersol, and ionamine colours may be dyed in combination.

DIRECTIONS FOR DYEING

In all cases, first scour and wet out the acetate silk material by working for 20 minutes in a bath containing 2 lb. soap and 2 pints ammonia per 100 gallons at 120° F. (50° C.). Rinse in water as soft as possible.

Duranol Dyestuffs and Dispersol Yellow 3G Paste

Process 1. Stir up the dyestuff paste with a little water, and add to the lukewarm dyebath at 110° F. (45° C.) preferably through a fine sieve. Gradually raise the temperature to a maximum of 175° F. (80° C.) and maintain at this temperature for from 20 to 30 minutes.

Note. Duranol Blue G. Paste does not exhaust as completely as the remaining members of the series, and where full shades are concerned requires dyeing a somewhat longer time at the maximum temperature.

Ionamine Dyestuffs

Process 2. Dissolve the dyestuff in warm water, not above 175° F. (80° C.). Dye as directed for Process 1, with the addition to the bath of 1–2 per cent. formic acid (80 per cent).

Applicable to the dyeing of all ionamines.

Process 3. As Process 2, but with the addition of 1- 2 per cent. soda ash in place of formic acid.

Ionamine A is preferably dyed by this process.

In addition, Ionamines MA, B, and H may be dyed by it, but not the remaining ionamines.

Process 4. Rinse the material, dyed according to Process 2 or 3, and treat for 20 minutes in a cold bath containing per 100 lb. material :

> 5 lb. sodium nitrite,
> 8 pints hydrochloric acid (32° Tw.).

Rinse well and develop for half-an-hour at the appropriate temperature in a bath containing :

> 5 lb. developer (see next page).

Experience has shown that an excess of developer, as recommended, is essential for good results. An appreciable amount remains unused in the bath, hence, if further lots of material are to be developed, it is economical to keep the bath standing and replenish

with smaller quantities of developer. For every further 100 lb. material developed in the standing bath there will be required only 2 lb. beta-oxy-naphthoic acid or beta naphthol.

Applicable to :

Ionamine MA	Ionamine H
Ionamine B	Ionamine L Paste
Ionamine GA	Ionamine A

DURANOL COLOURS OR DISPERSOL YELLOW 3G IN COMBINATION WITH IONAMINES

Dye together, according to Process 2 or 3, whichever is appropriate to the ionamine or ionamines employed.

DEVELOPERS

1. BETA-OXY-NAPHTHOIC ACID

A. Dissolve 5 lb. beta-oxy-naphthoic acid in 3 gal. of boiling water by adding to it half its weight of soda ash. Pour this solution into the developing bath at 120° F. (50° C.), and slightly acidify by adding 6–7 pints of acetic acid (30 per cent.).

We have put on the market an additional developer—Beta-oxy-naphthoic acid S, which is soluble in water, and we advise the use of this product in all cases where any difficulty is experienced with beta-oxy-naphthoic acid itself.

B. Dissolve 5 lb. beta-oxy-naphthoic acid S in 4 gal. of boiling water and pour the solution into the developing bath at 120° F. (50° C.), which is then slightly acidified by the addition of $3\frac{1}{2}$ pints acetic acid (30 per cent.).

2. BETA NAPHTHOL

Make 5 lb. beta naphthol into a thick uniform paste with water, add $3\frac{3}{4}$ lb. or $2\frac{1}{4}$ pints ($\frac{3}{4}$ times its weight) of caustic soda 76° Tw., stir well and then add hot water, while stirring, until dissolved. Use this developing bath at a temperature of 60–70° F. (15–20° C.) without addition of acid.

CELLUTYL COLOURS

These are a special selection of the best dyes possessing a direct affinity for cellulose-acetate silk. Many of these colours have been replaced by either duranol or ionamine dyestuffs, but the following are still used considerably in the dyeing of this type of artificial silk.

Cellutyl Yellow C
Cellutyl Sky Blue

These colours are dyed from a dyebath containing from 10–30 per cent. of common salt with or without the addition of formic or acetic acid.

Cellutyl Fast Blue

This colour is dyed with an addition of from 1–5 per cent. of acetic acid. It can be after-treated in a fresh bath with 1–3 per cent. bichrome and 1–3 per cent. formic acid when violet shades of excellent fastness are produced.

SCROOPING ARTIFICIAL SILKS

The object of scrooping is to impart a particular feel or handle to the material similar to that of natural silk. It is carried out by working the dyed material first in a soap bath, and then in a bath acidified with formic or tartaric acid. The goods are dried without rinsing. Such a treatment, while not affecting some dyestuffs, effects a considerable change of shade in others. In addition to change in shade, some dyestuffs may " bleed " in the acid bath.

When dyeing material for scrooping, it is usual to employ as far as possible, colours which withstand the treatment. In many cases, this is not practicable as a certain colour may be used on account of its level dyeing properties and yet not be entirely fast to scrooping. In all cases of dyeing for scroop, it is usual to pattern up from a skein which has been subjected to a similar treatment to that which will be finally given to the bulk.

Where soap has not been used for dyeing, then it is necessary to work the silk for about 20 minutes in a lukewarm soap bath containing 5 lb. soap per 100 gallons.

After hydro-extracting, the silk is given a treatment for 20 minutes in a cold acid bath made up as follows—

1 lb. to 8 lb. tartaric acid, or
1 lb. to 8 lb. formic acid
per 100 gallons liquor.

according to the required degree of " scroop."

Tartaric acid being non-volatile is superior to formic acid in that the scroop is more permanent. It is, however, somewhat expensive, but the cost can be lessened by the use of a proportion of formic acid.

THE DYEING OF UNION FABRICS

Mixed fabrics containing cotton, wool, or natural silk, together with viscose or acetate artificial silks, can be dyed to give solid shades. With wool or silk mixed with either viscose or acetate silk, or with mixtures of cotton and acetate silk, contrasting effects can be obtained often by a one-bath process. In this way many novel and interesting dyed fabrics can be produced, the contrast being obtained either by the production of two coloured effects or by leaving one of the materials undyed. The following brief notes, together with lists of suitable colours will serve as a guide to the dyeing of these various materials.

COTTON AND VISCOSE

The dyeing of solid shades on these two materials is very important with certain classes of goods, notably hosiery, which often consists of viscose with cotton tops and feet. On unmercerized cotton and viscose materials, the direct colours have a tendency to dye viscose a heavier shade than the cotton. This position is reversed when dyeing the prevailing pale shades on mercerized cotton and viscose hose.

DIRECT COLOURS CAPABLE OF DYEING SOLID SHADES ON UNMERCERIZED COTTON AND VISCOSE

The following are very suitable for dark and light shades :

Chrysophenine G	Chlorazol Fast Orange G
Chlorazol Fast Orange D	Chlorazol Fast Brown RK

The following colour is very suitable for shading the cotton :

Chlorazol Fast Yellow FG

The following are useful for moderately dark shades :

Chlorazol Fast Orange R	Chlorazol Blue RW
Chlorazol Fast Red K	Chlorazol Black FFH

The following are suitable only for light shades :

Chlorazol Fast Yellow 5GK	Chlorazol Blues B, RW, and 2R
Chlorazol Fast Yellow B	Chlorazol Azurine G
Chlorazol Yellow GX	Chlorazol Fast Blue 2BN
Chlorazol Fast Yellow NX	Chlorazol Sky Blues FF and GW
Titan Yellow G	Chlorazol Dark Green PL Conc.
Chlorazol Fast Orange AG	Chlorazol Orange Brown X
Chlorazol Fast Scarlet 4BS	Chlorazol Browns LF, M, PB, B, G,
Chlorazol Fast Pink BK	GR, and GN Extra
Chlorazol Fast Red K	Chlorazol Drab RH
Chlorazol Pink Y	Chlorazol Fast Black BK
Chlorazol Fast Rubine LF	Chlorazol Blacks SD, E Extra, BH,
Chlorazol Fast Helio BK	LF, and GF
Chlorazol Violets N, WBX, and R	Vulcan Black 2 GW
Chlorazol Dark Blue B	

WOOL AND VISCOSE

A selection of colours from the following lists will enable the dyer to choose those suitable either for solid shades or contrasting colour effects. By selecting neutral dyeing acid colours and suitable direct colours, both fibres can be satisfactorily dyed by a one-bath process.

DIRECT COLOURS FOR DYEING VISCOSE WHICH DO NOT STAIN WOOL

Dyed at 160° F. (70° C.) with the addition of Glauber's salt and 0·5 per cent. soda.

Chlorazol Fast Yellow B	Chlorazol Brilliant Sky Blue GW
Chlorazol Yellow GX	Chlorazol Blue B

Chlorazol Fast Orange D
Chlorazol Pink BK
Chlorazol Fast Scarlet 4BS
Chlorazol Fast Eosine B
Chlorazol Sky Blue FF

Chlorazol Fast Blue 2BN
Chlorazol Violets R, WBX, and N
Chlorazol Brown PB and LF
Chlorazol Drab RH
Chlorazol Black BH and N

NEUTRAL DYEING ACID DYESTUFFS SUITABLE FOR DYEING WOOL-VISCOSE MIXTURES

Dyed at the boil without addition.

Citronine Y conc.
Metanil Yellow Y
Acid Orange IV
Acid Orange G
Coomassie Milling Scarlet G
Milling Scarlet 5B
Cloth Red G
Fast Acid Violet 2R
Coomassie Violet R
Coomassie Navy Blue G

Coomassie Navy Blue GNX
Coomassie Navy Blue 2RNX
Disulphine Blue A
Disulphine Green B
Coomassie Green SS
Coomassie Fast Black B
Naphthalene Black 12B
Naphthalene Black D
Coomassie Blue Black

ACID DYESTUFFS WHICH DO NOT STAIN VISCOSE EFFECT THREADS

Dyed at the boil in a 3 per cent. sulphuric acid bath with the addition of 10 per cent Glauber's salt.

Acid Yellow 79210
Lissamine Fast Yellow 2G
Naphthol Yellow FY
Orange 2G
Acid Scarlet 5/0
Milling Scarlet 5B
XL Carmoisine 6R
Azo Geranine 2G
Azo Geranine B
Carmoisine WS
Coomassie Violet AV
Coomassie Acid Blue RL
Lissamine Blue B

Alizarine Celestol B
Indigo Extract L Paste
Indigo Carmine X
Coomassie Green SS
Alizarine Cyanine Green G. Conc.
Naphthol Green B 9211K
Acid Green G
Disulphine Green B
Lissamine Green V Conc.
Coomassie Wool Black ESNC
Naphthol Black L
Naphthalene Blue Black C
Naphthalene Black ESNC

The following colours just tint Viscose Effect Threads

Acid Scarlet R
Cardinal Red 3B
Lissamine Violet 2R
Fast Acid Violet 79446
Wool Blue 3R
Pure Soluble Blue

Lissamine Navy Blue G
Disulphine Blue V
Disulphine Blue A
Coomassie Navy Blue G
Naphthalene Black 12B
Coomassie Fast Black

CHROME MORDANT DYESTUFFS FOR DYEING WOOL WHICH DO NOT STAIN VISCOSE EFFECT THREADS

Dyed at the boil with the addition of 1–5 per cent. acetic acid, exhausted with 1 per cent. sulphuric acid and after-chromed with 1–2 per cent. bichrome.

Alizarine Yellow WS
Khaki Yellow WN Paste

Alizarine Cyanine Green G Conc.
Chromanthrene Green N

Solochrome Yellow Y
Alizarine Yellow L
Alizadine Orange M Paste
Solochrome Red B
Alizadine Brown R
Solochrome Brown MO
Solochrome Violet R

Era Chrome Olive MGG Paste
Era Chrome Dark Blue B
Fast Chrome Blue R
Carmoisine L 9156K and WS
Solochrome Black PBG, A, 6B,
    T and HS

Natural Silk and Viscose

The dyeing of natural silk and viscose mixtures is carried out by means of the same colours as used for dyeing wool-viscose material. In addition, we append a list of direct cotton colours, which will dye viscose and leave natural silk white.

Direct Cotton Colours for Dyeing Viscose which do not Stain Natural Silk

Dyed at 120° F. (50° C.) with the addition of 2 per cent. borax. Glauber's salt is added as required.

Chlorazol Fast Yellow B
Chlorazol Yellow GX
Chlorazol Fast Orange D
Chlorazol Fast Scarlet 4BS
Chlorazol Fast Eosine B
Chlorazol Fast Pink BK
Chlorazol Violet R
Chlorazol Fast Blue 2BN

Chlorazol Blue B
Chlorazol Sky Blue FF
Chlorazol Brilliant Sky Blue GW
Chlorazol Black BH (light and
    medium shades)
Chlorazol Drab RH
Chlorazol Brown PB
Chlorazol Brown LF

Mixtures of Cotton (or Viscose) and Cellulose-Acetate Silk

Owing to the fact that the majority of colours capable of dyeing cellulose-acetate silk have little or no affinity for cotton or viscose, and that the direct cotton colours, with few exceptions, have no affinity for cellulose-acetate silk, the production of contrasting effects is a comparatively simple matter. This marked difference in dyeing properties can also be made use of when dyeing solid shades.

Although the majority of direct colours do not dye cellulose-acetate silk, many of them stain it to a greater or less extent, a feature which would prove objectionable in practice. In order, therefore, to obtain perfect " whites " or pale contrasting shades when dyeing cotton or viscose with cellulose-acetate silk a specially selected range of direct colours have been put on the market under the name of CR chlorazol colours. These colours dye the cotton or viscose and leave the acetate silk unstained. They are indispensable for the production of white resist effects, and, in addition, their use is recommended for two-colour effects, as otherwise considerable trouble is likely to be experienced when the ordinary direct cotton colours are used owing to the staining of the Acetate silk, and

to the allowance which must be made for this staining, when matching up to shade.

The CR chlorazol colours should be used in the following way—

(a) *Before Dyeing.* The material should be cleaned in a solution of 2 per cent. soap and 2 per cent. ammonia, calculated on the weight of material, being worked for 15–20 minutes at a temperature of from 100–120° F. (40–50° C.), then rinsed, first in warm and finally in cold water.

(b) *Dyeing.* In the dyeing operation, a temperature of 175–185° F. (80–85° C.) should not be exceeded, otherwise there is a tendency for the acetate silk to become "blinded" (i.e. lose its lustre).

The volume of dye-liquor should not be less than twenty times the weight of the material, and, whenever possible, thirty times should be taken, as a reasonably dilute dye-liquor is advisable for the production of the best results.

For Resist Effects

The dyebath is made up with the CR chlorazol colour and salt or Glauber's salt only ; the material is entered and the temperature is brought slowly up to a maximum of 185° F. (85° C.), and dyeing is carried out at this temperature for ½–1 hour.

In order to obtain perfectly clear whites, it is advisable to give a final soaping, particularly when medium or dark shades have been dyed on the cotton or viscose silk.

For Two-colour Effects

The duranol, ionamine, and cellutyl colours can be used in conjunction with the CR chlorazol colours for the production of two-colour effects (see pages 262 to 266) ; the above colours will work together with the CR colours in the same bath in the majority of cases.

The dyeing of two-colour effects is carried out with the same addition to the dyebath as in the case of resist effects, except where otherwise stated. The same precautions with regard to dyeing temperature and dilution of the dyebath should be observed and the final soaping is an advantage for the production of clear effects on the acetate silk.

CR Chlorazol Colours

CR Chlorazol Fast Yellow B	CR Chlorazol Fast Blue 2BN
CR Chlorazol Yellow GX	CR Chlorazol Blue 3B
CR Chlorazol Fast Yellow NX	CR Chlorazol Fast Green
CR Chlorazol Fast Yellow FG	CR Chlorazol Brown PB
CR Chlorazol Fast Orange AG	CR Chlorazol Drab RH
CR Chlorazol Fast Orange R	CR Chlorazol Fast Brown No. 1

CR Chlorazol Fast Red K
CR Chlorazol Fast Pink BK
CR Chlorazol Fast Scarlet 4BS
CR Chlorazol Fast Eosine B
CR Chlorazol Fast Bordeaux LK
CR Chlorazol Violet R
CR Chlorazol Sky Blue FF
CR Chlorazol Sky Blue GW
CR Chlorazol Blue B

CR Chlorazol Fast Brown No. 2
CR Chlorazol Nigger Brown N
CR Chlorazol Black BH
CR Chlorazol Fast Black N
CR Chlorazol Black GF
CR Chlorazol Black
CR Chlorazol Black LH
CR Chlorazol Fast Grey

The following CR chlorazol colours are not materially affected by the diazotizing and developing process—

CR Chlorazol Fast Scarlet 4BS
CR Chlorazol Fast Oranges AG
   and R
CR Chlorazol Fast Yellows, B,
   FG, and NX

CR Chlorazol Fast Blue 2BN
CR Chlorazol Yellow GX
CR Chlorazol Fast Green

Cellutyl Union Blacks on Cotton (or Viscose) and Cellulose-Acetate Mixtures

Two union blacks—Cellutyl Union Blacks R and G—are on the market for dyeing this type of material and are especially valuable for hosiery dyeing. These colours require to be diazotized and developed in order to produce shades fast to light and washing. They are dyed according to the following formula—

The dyebath, heated to 120° F. (50° C.), is made up with 10 per cent. dyestuff, 2 per cent. soda ash, and 10–20 per cent. common salt. The material is entered and the temperature of the dyebath quickly brought up to 175° F. (80° C.) and dyeing carried out at this temperature for 1 hour, further additions of 30 per cent. salt being made. It is important to keep the ratio of dye-liquor to material as low as possible.

After dyeing, the material is rinsed and diazotized for 20 minutes in a cold bath containing 2½ per cent. sodium nitrite and 7½ per cent. hydrochloric acid (32° Tw.).

After diazotization, the material is again rinsed and developed for ¼ hour at 120° F. (50° C.) in a bath containing 5 per cent. beta-oxy-naphthoic acid, acidulated with acetic acid. This latter point is of considerable importance.

(The beta-oxy-naphthoic acid or the soluble " S " brand is made up in accordance with the formula given on page 265.)

The material is finally rinsed and soaped for 20 minutes at 120° F. (50° C.) in a bath containing 2 lb. of soap per 100 gallons water.

Sulphur Colours on Cotton (or Viscose) and Cellulose-Acetate Material

By means of a special process,* it is possible to dye sulphur blacks

* B.P. 238721.

and other sulphur colours on mixtures of the above materials in such a manner that the cellulose-acetate silk is left white (or only tinted) and is not saponified by the alkaline dyebath.

The dyebath is made up with—

3 parts sulphur colour dissolved by boiling with
6 parts sodium sulphide crystals in
160 parts water.
3 parts ammonium sulphate, previously dissolved in
40 parts water, are then added and the temperature adjusted to 176° F. (80° C.).

The material is padded in this solution and then thoroughly rinsed and dried.

Suitable sulphur colours for use with this process are—

Thionol Brown P.   Thionol Green B
Thionol Brown B   Thionol Green 2G Conc
Thionol Corinth GX   Thionol Black GSX Conc.

DURANOL AND VAT COLOURS ON VISCOSE AND CELLULOSE-ACETATE MATERIAL

There is some demand for fast shades on this type of material, and as it is a demand which is rapidly extending we have recently introduced a special process which enables vat colours to be applied to the viscose in place of the ordinary CR chlorazol colours.

The difficulty hitherto has been due to the fact that the caustic soda necessary for the application of the vat colours saponifies the acetate silk. This difficulty can be overcome by restricting the dyeing temperature and adding beta-naphthol to the bath to neutralize any excess of caustic soda. This prevents saponification, and yet at the same time the colour is not thrown out of solution. Our duranol colours on the fibre withstand the reducing action of the vat bath.

The details of the process are as follows--

First Bath. The duranol colours are applied to the cellulose-acetate in the customary manner.

Second Bath. For 100–120 gallons dye-liquor.

BETA NAPHTHOL SOLUTION

4–8 pints caustic soda 76° Tw.
$1\frac{3}{4}$–$3\frac{1}{2}$ lb. B. Naphthol   } Total amounts.
$1\frac{1}{2}$–4 lb. hydrosulphite powder

Half of the above total amount of caustic soda is used to dissolve the beta naphthol in the usual way by pasting and pouring on hot water.

COLOUR SOLUTION

The requisite amount of colour is reduced in a separate vessel, using the following proportions—

> 1 lb. colour paste
> 2 gallons water 120°–130° F. (50°-55° C.).
> ½ pint caustic soda 76° Tw.
> 4 oz. hydrosulphite powder.

Any caustic soda and hydrosulphite now remaining from the "total amounts" given above are added to the dyebath, followed by the beta-naphthol solution, and then the reduced colour solution (after 15–20 minutes reduction).

DYEING IN THE SECOND BATH (VAT BATH) IS CARRIED OUT COLD

The material can be oxidized in the usual way and then soaped at 160–175° F. (70–80° C.).

The following of our vat colours are suitable for use by this process—

Duranthrene Yellow G Extra	Duranthrene Brilliant Violet R
Duranthrene Golden Orange Y	Duranthrene Violet 2R
Duranthrene Golden Orange 2RT	Duranthrene Olive R
Duranthrene Red 5G	Duranthrene Blue GCD
Duranthrene Red BN	Duranthrene Green 2B
Duranthrene Red Violet 2RN	

WOOL AND CELLULOSE-ACETATE SILK

The dyeing of wool and cellulose-acetate silk is a problem which has yet to be solved. The selection of suitable colours presents no special difficulty, but when dyeing, acetate silk must not be heated to temperatures higher than 175° F. (80° C.), and at this temperature it is impossible to dye wool satisfactorily with the majority of dyestuffs. A certain amount of wool-acetate silk mixture, is, however, being dyed, usually in the form of yarn where the two fibres are intimately mixed together and where a certain unlevelness on the wool is not noticeable.

The following list of acid colours which will dye wool at 175° F. (80° C.) and leave acetate silk unstained, should be of assistance when dyeing this type of material.

ACID COLOURS ON WOOL AT 175° F. (80° C.) WHICH DO NOT STAIN CELLULOSE-ACETATE

Lissamine Fast Yellow 2G	Coomassie Navy Blue 2RNX
Acid Yellow 79210	Indigo Carmine X
Naphthol Yellow FY	Lissamine Blue B
Acid Scarlet 4R Extra	Lissamine Navy Blue G
Coomassie Scarlet 9012K	Alizarine Delphinol BDN
Azo Geranine B	Disulphine Blue A
Carmoisine WS	Disulphine Blue V

Carmoisine L 9156K	Fast Acid Blue RH
Fast Red EAS	Disulphine Green B
Cardinal Red 3B	Acid Green G
Lissamine Red 6B	Lissamine Green V Conc.
Lissamine Violet 2R	Coomassie Green SS
Coomassie Violet AV	Naphthalene Blue Black C
Coomassie Acid Blue RL	Naphthalene Black ESNC

DYEING SOLID SHADES OF BLACK ON WOOL AND CELLULOSE-ACETATE MIXTURES

Solid shades can be obtained by means of Cellutyl Union Blacks No. 1 and No. 2.

These colours are dyed with the addition of 2 per cent. formic acid, dyeing being carried out for $\frac{3}{4}$ hour at 80° C. The goods are then rinsed thoroughly and diazotized with—

3 per cent. sodium nitrite

and 10 per cent. hydrochloric acid (32° Tw.)

for $\frac{1}{2}$ hour cold.

After diazotizing, the material is again rinsed thoroughly and developed with 8 per cent. beta-oxy-naphthoic acid for $\frac{1}{2}$ hour at 120° F (50° C.), washed and dried.

(The development with beta-oxy-naphthoic acid is carried out according to the directions given on page 265.)

THE PRINTING OF ARTIFICIAL SILKS

VISCOSE, NITRO, AND CUPRAMMONIUM SILKS

As these silks consist simply of regenerated cellulose in a slightly modified form, they can be printed with direct, basic, mordant, vat, and sulphur colours in a similar manner to cotton. At the same time, they possess certain peculiarities owing to differences in the physical structure of the fibre.

The direct colours are applied by dissolving the colour along with glycerine in condensed water and phosphate of soda and adding a suitable thickening, for example British Gum and/or wheat starch, printing, drying lightly, and steaming for 1 hour without pressure in as damp an atmosphere of steam as is possible. These colours give bright shades which are faster than when applied upon ordinary cotton. The following colours are pre-eminently suitable for this purpose—

Chrysophenine GP	Chlorazol Blue 2R
Chlorazol Fast Orange AG	Chlorazol Fast Helio BK
Chlorazol Fast Red K	Chlorazol Fast Black BK
Chlorazol Fast Pink BK	Chlorazol Black GF
Chlorazol Fast Red FG 9202K	Chlorazol Black SD
Chlorazol Fast Blue 2BN	

The last three are particularly useful as greys or toning shades.

The basic colours are applied in the customary manner, using

tannic acid as a fixing agent and, as no special complication arises, the printing pastes are the same as would be used for ordinary cotton fabrics. The same holds for all chrome mordant colours.

In the case of vat colours, any type of recipe which is suitable for the colour in question can be used with advantage. Care, however, must be taken in the subsequent washing off. As the viscose fibre is liable to be softened when wetted out in water, precaution must be taken to prevent undue strain being exerted upon the fibre during the process of oxidation of the vat colour after ageing.

DISCHARGING OF VISCOSE DYED GROUNDS

This question presents no more serious difficulty than is encountered in the case of the discharges upon cotton coloured grounds, and where the colour is chemically suitable the basic rongalite discharge style proceeds smoothly and easily, and we encounter on the market very many beautiful examples of the multi-coloured effects which can be obtained by this particular style.

CELLULOSE-ACETATE SILK

The physical and chemical properties of cellulose-acetate silk differ so markedly from those of the other types of artificial silks that, as with the dyeing, so the printing of this material is an entirely new art and one which is still largely in the experimental stage.

The physical structure of this material consists really of hard, rod-like fibres, which are very impenetrable, and this causes a certain amount of difficulty in the obtaining of printed patterns upon the fibre. As a general rule, soft thickenings of the nature of British gum or *Gum Tragacanth* are to be recommended for conveying the colours into the fibre.

Cellulose-acetate silk may be printed in two ways—

(a) Direct printing.
(b) Printing using a process of saponification.

DIRECT PRINTING

In this case most of the colours are of a special chemical nature, being such that they have direct affinity for the acetate cellulose ; the two main classes are ionamine colours and duranol colours

The former are printed by a general recipe consisting of ionamine colour paste or powder mixed with water and a suitable amount of a well-calcined British gum thickening. Fixation is obtained by steaming the colours at 212° F. (100° C.), in the dry steam for ½ hour. It can then be washed off in lukewarm water. Typical examples of this class of colours are Ionamine A, Ionamine B, Ionamine MA, Ionamine GA, and Ionamine Red KA. In all steaming operations

it is absolutely essential that the humidity of the steam should not be excessive since this type of artificial silk is very liable to become " blinded " if exposed to a hot, damp atmosphere ; no derogatory effect, however, takes place, even on prolonged steaming, provided that the condition of the steam is dry.

The other class of colours pre-eminently suitable for cellulose-acetate printing are the duranol colours. They are of the highest degree of fastness to light and washing, and can be strongly recommended where these qualities are essential. They are in paste form and are applied by diluting the paste to the necessary colour concentration with *Gum Tragacanth* solution and water. After printing the goods are steamed for half-an-hour in dry steam and washed off. This range of colours consists of—

Dispersol Yellow 3G Paste	Duranol Blue G Paste
Duranol Red 2B Paste	Duranol Violet 2R Paste
Duranol Red G Paste	Duranol Black 2B Paste
Duranol Orange G Paste	

Certain cellutyl colours can also be employed for printing, and, in the case of Cellutyl Fast Light Green B and Y, Cellutyl Sky Blue, Cellutyl Bright Red, and Acronol Brilliant Blue, the colours are much faster to light on acetate silk than they are on cotton.

In preparing the printing paste for these colours, the dyestuff is dissolved in 10 per cent. acetic acid, and thickened with such media as *Gum Tragacanth* or British gum. After printing, the only process necessary is steaming, the fixation in tartar emetic not being requisite.

Basic colours may be applied in a similar manner, among which may be mentioned—

Methyl Violet 2B	Tannin Pink C
New Methylene Blue S	Safranine T Conc.
Rhodyle 4G	

The vat colours also may be applied to the cellulose-acetate silk, in which case it is desirable to use a method employing weak alkalis We would recommend the following recipe for this purpose—

10–15% vat colour paste	2½% solution salt
3% glycerine	7–8% Formosul
4% caustic soda 76° Tw.	60–65% British gum thickening
5% soda ash	(3 lb. per gall.)
5% potassium carbonate	

After printing the goods are aged for 3–5 minutes at 214° F. in a Mather & Platt ager, washed off in running water and soaped at 180° F.

Sulphur colours, for example,

Thionol Printing Black No. 2
Thionol Brown GD
Thionol Green B

may be applied with good results by methods similar to those indicated above for the vat colours.

The chrome mordant colours may also be applied to cellulose-acetate silk, using an addition of chromium acetate, and light or medium shades may be so produced.

SAPONIFICATION PROCESS

• The direct cotton colours, with an odd exception, have no direct affinity for cellulose-acetate silk in its normal state, but they may be printed by a process of local saponification. Here caustic soda is added to the printing paste and applied to the fabric during the steaming operation. Saponification of the cellulose-acetate takes place with the formation of regenerated cellulose, and for this part of the fibre the direct colour has a definite affinity. The printing colour to be used in this connection is made up as follows—

> 2 grm. of dry colour dissolved in
> 40 cc. distilled water and
> 1 grm. phosphate of soda.

This mixture is added to 80 cc. gum arabic thickening (60 per cent.), and finally 20 cc. caustic soda 76° Tw. added. The goods are printed, aged for ½ hour at 214° F., and washed off. The difficulty with this process is that the physical and chemical characteristics of the acetate silk are altered locally, and in the case of very heavy blotch patterns there would be a serious loss in weight owing to the saponification of the cellulose acetate.

DISCHARGING OF CELLULOSE-ACETATE SILK

Owing to the extent of the use of acetate silk for dress and other fabrics, multi-coloured effects are absolutely essential, and one of the greatest difficulties in the past has been in the procuring of coloured discharge effects upon dyed acetate silk grounds. When a direct cotton colour dischargeable by rongalite is applied to an ordinary cotton fabric and printed with a discharge paste consisting of the sulphoxylate formaldehydes, e.g. Rongalite C, Formosul, etc.. a pure white is obtained on subsequent ageing and washing, but if such a colour is applied to cellulose-acetate and similarly printed and after-treated, the discharge effect is very imperfect. It has been found that this really is due to the different physical nature of the fibre. There is great difficulty in penetrating the individual acetate-silk fibre and, even where penetration takes place, a further difficulty occurs in washing out the reduction products of the ground shade, with the result that perfect discharges were rarely possible. It has now been found that by the addition of sulphocyanides of metals to the rongalite printing pastes the penetration is greatly assisted, and where the colour is of such a chemical nature that a

perfect discharge should take place using rongalite, this result is obtained by the aforementioned addition. (A provisional patent has been granted for this process.) We find that the calcium thiocyanate is the best salt to use, and it has no detrimental effect upon the strength or nature of the fibre. The addition of the sulphocyanide may also be made to a basic rongalite discharge printing colour and increased " cutting " of the ground shade is obtained, though the basic colour itself is dulled slightly by this addition.

By this means it has been found possible to discharge what have been considered in the past as undischargeable colours. For instance, Ionamines A, MA, GA, and Red KA, as direct shades are discharged to a perfect white by this means and Ionamine B and GA in the developed state will also yield perfect whites.

Other colours suitable for this discharge process are—

Cellutyl Fast Yellow C	Cellutyl Fast Red D
Cellutyl Fast Golden Yellow	Cellutyl Sky Blue
Cellutyl Orange 2R	Acronol Brilliant Blue

Colours of the type of Methyl Violet 2B or 10B, Cellutyl Bright Red, Bismarck Brown R100s, can also be used with discretion for obtaining ground shades which, on printing with rongalite sulphocyanide discharge, give perfect whites.

COTTON-VISCOSE, COTTON-CELLULOSE-ACETATE, AND VISCOSE-CELLULOSE-ACETATE FABRICS

(1) *Cotton-Viscose.* Since the affinity of the various classes of colours for viscose is similar to that for cotton, no special precaution need be taken or any special range of colours need be selected for the obtaining of solid shades upon union fabrics consisting of viscose and cotton.

(2) *Cotton-Cellulose-Acetate.* Owing to the entirely different chemical nature of these fibres and owing to the fact that widely diverse types of colours can be applied to each fibre, difficulties arise in the production of either solid or two-colour effects. In the case of solid shades, it is essential to apply a colour to the acetate silk which will have no staining effect upon the cotton, and vice versa. The effect of solid shades is, therefore, produced by using mixtures of duranol and CR colours, of such a nature that the CR colour on the cotton is approximately the same shade and depth as the duranol colour on the acetate silk, for example, by printing

> 5·0% Duranol Red 2B paste and
> 1·5% CR Chlorazol Fast Pink BK

a solid pink is obtained.

An orange is produced by using a mixture of—

> 5·0% Duranol Orange G Paste, and
> 1·5% CR Chlorazol Fast Orange AG

and a solid violet is obtained from the following mixture—

> 5·0% Duranol Violet 2R paste,
> 1·0% CR Chlorazol Fast Pink BK
> 0·5% CR Chlorazol Fast Helio BK

In all these colours the direct CR colour is dissolved in condensed water, added with glycerine to a thickening consisting of British gum, and the whole warmed up. When a perfect solution is obtained the paste is cooled down and the duranol colour is added. After printing, the goods are lightly dried, steamed one hour without pressure at 212° F. in a fairly dry atmosphere, and washed in running water. By this means the colours which have become attached mechanically to the opposite fibres are removed, leaving a solid effect.

When solid effects by the use of basic colours upon cotton-cellulose-acetate unions are desired, the basic colour must be princed with the addition of tannic acid, so that complete fixation may result upon the cotton portion of the fabric. The resultant shade upon the acetate silk is, however, duller than is the case when the basic colour is applied direct to the silk alone. As a general rule, this type of solid effect is not in great demand.

Unique two-colour effects upon cotton-acetate silk union may be produced by taking advantage of the affinity of the C.R. colour for cotton, and the duranol colour for the acetate silk, and where colours of a contrasting shade are employed, two-colour " shot " effects can be produced. The printing recipe for these colours is the same as the one for producing the solid effects, and the following CR colours are particularly suitable for this style—

CR Chlorazol Yellow GX	CR Chlorazol Fast Blue 2BN
CR Chlorazol Fast Pink BK	CR Chlorazol Fast Brown PB
CR Chlorazol Fast Orange R	CR Chlorazol Drab RH
CR Chlorazol Fast Scarlet 4BS	CR Chlorazol Dark Green PL
CR Chlorazol Fast Black BH	CR Chlorazol Fast Red K

(3) *Viscose-Cellulose-Acetate Silk.* Since the properties of viscose are similar to those of cotton, the remarks made in Section 2 (cotton-acetate silk unions) will hold in this case equally as well.

Although the general effect of dyestuffs on regenerated cellulose artificial silks—nitro, cuprammonium, and viscose—is pretty constant, there may be some little differences in phases that have not been fully considered by all those connected with the dyeing industry. In this respect, the following notes from *Dyeing of Viscose with Direct Cotton Dyestuffs*, introduced by the permission of Messrs. Courtaulds, Ltd., should be of particular interest.'

THE DYEING OF VISCOSE WITH DIRECT COTTON DYESTUFFS

It has been stated on page 255 that viscose may be dyed like cotton. This is not true except in a very general sense, because

many direct cotton dyestuffs such as B.H. Black, which have met with general acceptance for the dyeing of cotton, have proved utterly unsuitable for the dyeing of viscose. It is also an accepted axiom in dyeing that a dyestuff which dyes slowly gives the most even results, whereas experience with viscose has shown that those dyestuffs which dye rapidly give the most even results, whilst the slow dyeing ones give the most uneven results.

There are four properties possessed by those direct cotton dyestuffs which give the most even results on viscose, and four simple tests by which those properties may be determined.

(1) Those dyestuffs possessing a high number as determined by a capillary test (details below) give the most even results.

(2) Even dyeing dyestuffs dye on at a rapid rate.

(3) Viscose dyed with even dyeing dyestuffs when boiled in a soap bath for half an hour along with an equal weight of undyed viscose loses colour which dyes on the undyed viscose. The nearer the shade of the dyed and undyed viscose approximate to each other after boiling with soap, the more suitable the dyestuff for viscose. Viscose dyed with uneven dyeing dyestuffs when submitted to the boiling soap test does not lose much depth of shade whilst the white viscose is hardly stained.

(4) Even dyeing dyestuffs require the least Glauber's salt as assistant in the dyebath: experience has shown that the less Glauber's salt used, the more even is the viscose.

These properties exert the greatest influence in compound shades, because some dyestuffs—not possessing the above properties—may give a fair result in a self shade, but will give a very bad result when used with other dyestuffs in compound shades.

METHODS OF MAKING THE ABOVE TESTS.

1. If equal lengths of viscose thread are hung for 15 minutes in dyebaths of Chrysophenine and Sky Blue FF at the same temperature, it will be found that the Chrysophenine rises up the thread but a short distance, whereas the Sky Blue FF rises up the thread a considerable distance. If the amount of undyed thread is measured after fifteen minutes a number may be obtained for each direct cotton dyestuff. This procedure gives high numbers to low rising dyestuffs and low numbers to high rising dyestuffs.

Experience has shown that the high number direct cotton dyestuffs like chrysophenine dye viscose evenly, whilst the low number direct cotton dyestuffs like Sky Blue FF dye viscose unevenly.

By determining this suction number under standard conditions, it is possible for a dyer to say at once whether a direct cotton dyestuff will give an even or uneven shade on viscose and which direct cotton dyestuffs are suitable for mixing one with the other for the production of compound shades.[1]

. [1] These suction numbers, determined by C. M. Whittaker, B.Sc., should be of great value for the dyers of viscose silks.—T. W.

Experience has proved two facts—

(*a*) Compound shades should be dyed with direct cotton dyestuffs of as near the same number as are available ; the higher the numbers, the more even the shade, therefore the high number dyestuffs when available must always be given the preference.

(*b*) The mixing of high number direct cotton dyestuffs with low number direct cotton dyestuffs must be avoided, because such a mixture will give a more uneven result than a mixture of low number direct cotton dyestuffs.

The numbers given to the direct cotton dyestuffs in the list below were determined under the following standard conditions—

> 400 c.c. water
> 0·4 grm. dyestuff
> 0·2 grm. soap
> 1 grm. Glauber's salt

Duration of test fifteen minutes at 60° C.

Total length of dry viscose twist used 25·5 cm.

Length of twist above level of liquor 22·3 cm.

The figures given in the list represent the length in centimetres of white twist left after fifteen minutes' suction. As a matter of working practice, one can more accurately measure the white portion of the twist, because measuring the dyed twist introduces the uncertain factor of the dye liquor level. If a double length of viscose twist is used, this may be hung over a piece of glass rod or string arranged at the appropriate height.

All comparative tests must be made on the same twist ; it is advisable therefore to reserve a suitable quantity of the same twist for use in these tests.

DIRECT COTTON DYESTUFFS WITH DYEING NUMBERS ATTACHED

REDS

	Whittaker's Numbers		Whittaker's Numbers
Benzo Fast Bordeaux 6BL	12	Chlorazol Fast Bordeaux LK	9½
„ , Light Scarlet 4BL	9½	„ „ Eosine B	11
Bensoform Scarlet B	15	„ „ Pink BK	8
Benzopurpurine 4B	15	„ „ Red FG	11
„ 10B	13½	„ „ Red K	12
Chloramine Fast Scarlet 2B	10	„ „ Rubine LF	8
„ „ Red T	12	„ „ Scarlet 4BS	10½
Chlorantine Fast Bordeaux 2BL	9½	Congo Rubine	9
„ „ Red 7BL	9	Diamine Fast Scarlet 8BS	11
„ „ Rubin RL	10	Diazo Brilliant Scarlet BA Extra	8½

REDS (*contd.*)

	Whittaker's Numbers		Whittaker's Numbers
Diaze Fast Red 5BL . .	8	Erica G3B . . .	10
,, ,, ,, 7BL . .	8½	,, GB . . .	10
Diazogene Red B . .	19	Paramine Fast Bordeaux B .	18
Diazo Geranine B Extra .	18½	,, ,, Pink B .	13
,, Rubine . . .	11	Rosanthrene Fast Bordeaux—	
Diphenyl Bordeaux B Conc. .	12	2BL	10½
,, Fast Bordeaux BC .	12½	BL	9½
,, ,, ,, G .	16	Toluylene Red . . .	11
,, ,, Red B . .	12½		

BLUES

Benzo Fast Blue 2GL . .	9	Diazo Fast Blue 2RW . .	10
Benzoform Blue G Extra .	15	,, ,, ,, 6GW Conc. .	10
Brilliant Fast Blue 3BX .	9	,, ,, ,, 4GW Conc. .	10
Chlorantine Fast Blue 2GL .	9	,, ,, ,, 2BW .	9½
,, ,, ,, RL .	9	,, Indigo Blue 4GL Extra .	12
Chlorazol Azurine G . .	11½	,, ,, ,, 2RL .	9½
,, Blue B . .	12	,, ,, ,, 3RL .	11½
,, ,, 3B . .	10	,, Sky Blue 3GL .	18
,, ,, 2R . .	8	Diphenyl Fast Blue BL Supra .	12
,, ,, RW . .	9	,, ,, ,, FB Conc .	8
,, Diazo Blue 2B . .	10	,, ,, ,, 2GL .	10
,, Fast Blue 2BN .	9	Formal Fast Blue B Conc. .	9
,, Sky Blue FF . .	9	,, ,, ,, R ,, .	10
Congo Fast Blue B . .	9½	Hexamineral Black Blue B .	9
Diamine Fast Blue F3G . .	10	Icyl Blue G . . .	12
,, ,, ,, CG .	9	Naphtogene Blue 2R . .	10
Diamineral Blue CVB . .	8½	,, Indigo Blue B .	10
Diaminogene Blue NB . .	8	,, Pure Blue 4B .	8
,, Sky Blue N .	18	Solamine Blue BF . .	9
Diazamine Blue BR . .	8	Triazol Light Blue 4GL .	8
,, ,, 2R . .	8		

ORANGES

Benzo Fast Orange 2RL .	9	Direct Fast Orange SE . .	9½
Chlorantine Fast Orange TRL .	9	Icyl Orange R . .	19
Chlorazol Fast Orange AG .	8	Pyramine Orange R . .	9
,, ,, ,, D .	9	Pyrazol Orange G . .	10
,, ,, ,, G .	19	,, ,, 2R . .	14
Congo Orange R . .	8½	Stilbene Orange 4R . .	10
Diamine Fast Orange ER .	9½	Triazogene Orange R . .	17½
Diazo Brilliant Orange—			
5G Extra . . .	12		
GR Extra . . .	19		

BROWNS

Benzo Brown BX . .	9½	Chlorazol Brown B . .	12
,, Fast Brown GL .	10	,, ,, G .	14½
Benzochrome Brown G .	10	,, ,, 2G .	10½
Benzoform Brown 4R .	16	,, ,, GM .	9½
Chloramine Brown OR .	13	,, ,, M .	13
Chlorantine Fast Brown 5GL .	10½	,, ,, PB .	9½
,, ,, ,, RL .	9	,, ,, LF .	9½

BROWNS (contd.)

	Whittaker's Numbers		Whittaker's Numbers
Chlorazol Drab RH . .	10	Dipheny Fast Brown GN Extra	9
Chlorazol Fast Brown LG .	10	Icyl Brown G . . .	16½
„ „ „ RK .	9	Paramine Brown B . .	14
Chromanil Brown 2G . .	13½	Pluto Brown GG . .	13½
Congo Brown G . .	17	„ „ R . .	15
Diamine Fast Brown G . .	10	Toluylene Fast Brown Bronze 3G .	8½
Diphenyl Brown 2BN Extra .	13½	Trisulphon Bronze B . .	9
„ Catechine G Extra .	9	„ Brown MB . .	9

GREENS

Benzoform Green FFL . .	10	Chlorazol Dark Green PL Conc	9
Brilliant Benzo Green B .	12½	„ Green G . . .	9
Chlorantine Fast Green BL .	11		

VIOLETS

Benzo Fast Helio 4BL . .	12	Chlorazol Violet WBX . .	9
„ „ „ 2RL .	18½	Diamino Brilliant Violet B .	15
Chloramine Violet FFB . .	9	„ „ „ 2R .	16
„ „ R . .	9	Diphenyl Fast Violet CB .	9
Chlorantine Fast Violet BL .	10	„ „ „ BV .	8
„ „ „ 4BL .	8	Icyl Violet B . .	12
„ „ „ 2RL .	8	Naphthamine Light Violet 2B .	18
Chlorazol Fast Helio BK .	18	Trisulphon Violet B . .	12
„ Violet N . .	10		

YELLOWS

Brilliant Benzo Fast Yellow GL	13½	Chrysophenine G . . .	19
Benzo Fast Yellow RL . .	17	Cotton Yellow G1 . . .	19
„ „ „ 4GL Extra	17	Diazo Fast Yellow G . .	19
Chlorantine Fast Yellow 4GL .	19	„ „ „ GG .	19
„ „ „ RL .	17	Oxyphenine GG . . .	8
Chlorazol Fast Yellow 5GK .	21	„ R . . .	8
„ „ „ B .	8	Paramine Fast Yellow 3G .	11½
„ „ „ R .	8	Primuline	20½

BLACKS

Chlorazol Black BH . .	9	Columbia Fast Black V Extra .	10
„ „ E Extra .	11	Direct Fast Black B . .	21
„ „ GF .	10	Formal Black G Conc. . .	10
„ „ FFH .	12½	„ „ R „ .	14½
„ „ LF .	8½	Icyl Blue Black 6B . .	16
„ „ DV .	9	Neutral Grey G . . .	10
„ „ SD .	21½	Vulcan Black 2GW . .	15
„ Fast Black BK .	17½	Oxydiaminogene OB . .	9
Columbia Fast Black G Extra .	10	Diaminogene Extra . .	11

Many of the dyestuffs in the above list are marketed under different trade names. In order to keep the list a reasonable size, the alternative names have not been included, but they may all be found in the "Colour Index" issued by the Society of Dyers and Colourists.

2. The most rapid dyeing direct cotton dyestuffs give the most even results on viscose. Those direct cotton dyestuffs with the highest numbers in the above list are the most rapid dyeing, whilst those direct cotton dyestuffs with the lowest numbers are the slowest dyeing.

It is absolutely essential for even results in compound shades to use dyestuffs which dye on at the same rate, and that is why it is such bad practice to mix high number and low number dyestuffs, because they dye on at different rates, and therefore give the most uneven results with the widest contrast in tone.

Dyeing differences in viscose vary in degree according to the make—the best makes show but slight dyeing differences, which may, in the majority of shades, be completely covered by a correct choice of direct cotton dyestuffs on the lines indicated in this Appendix. In no case should two makes of viscose be dyed together, but they should always be dyed separately.

It will be seen, therefore, that the best method of counteracting the variation in affinity, is to use rapid dyeing dyestuffs which dye the viscose before the variation in affinity has time to assert itself. On the contrary, the use of slow dyeing dyestuffs allows the variation in affinity to come into play with the inevitable result that the viscose with the stronger affinity comes out darker in tone.

If a rapid dyeing and high number dyestuff (Chrysophenine) is mixed with a slow dyeing and low number dyestuff (Sky Blue FF), to obtain a green, the result will be bad. The Chrysophenine dyes equally on to all the viscose, whilst the Sky Blue FF dyes more on to the viscose with the stronger dyeing affinity to the detriment of that possessing the weaker dyeing affinity. The end result must be therefore that the darker shade will be a blue-green, due to the preponderance of the Sky Blue FF, whilst the paler shade will be a yellow-green, due to the preponderance of Chrysophenine. A more uniform result will be obtained by substituting the Chrysophenine by one of the many low number direct cotton yellows, since there is not a suitable high number direct cotton blue.

The following method of testing enables one to decide whether a choice of dyestuffs is suitable or not by testing the relative rate of dyeing.

Make up sufficient dye liquor for six dye tests of a compound shade. Divide the dye liquor into six equal portions, in which dye equal weights of viscose under identical conditions of volume and temperature, but for periods of 5, 10, 15, 20, 25 and 30 minutes, or alternatively, 1, 2, 3, 4, 5 and 30 minutes. If the mixture under test consists of three high number dyestuffs, the hank dyed 5 minutes will be the same tone as the hank dyed 30 minutes, whilst the difference in depth will not be very marked. If the mixture under tests consists of three low number dyestuffs, the hank dyed 5

minutes will be much lighter in tone than the 30 minutes' hank, whilst the hanks will definitely grade in depth according to time of dyeing. If, however, the mixture under test consists of two high number and one low number dyestuff, the hanks will not only grade in depth but will vary in tone, and the low number dyestuff will predominate on the longer dyed hanks, because it is the slowest dyeing dyestuff. This, again, emphasizes why it is such bad practice to mix high number and low number dyestuffs together because they dye on at different rates.

3. If a skein of viscose is examined after being in the dye liquor for a very short period, it will be found that the outside threads are more dyed than the inside threads or those threads in the immediate neighbourhood of the lacings. It follows, therefore, that a direct cotton dyestuff which will, as the dyeing process proceeds, dissolve off the darker dyed threads and dye on to the lighter dyed threads will give the most level result by counteracting what happens in the first few minutes of dyeing, due to the mechanical impossibility of wetting the skeins uniformly when first immersed in the dye liquor. Experience has shown that the higher number direct cotton dyestuffs do this the more completely, whilst the low number direct cotton dyestuffs do not do this to any appreciable degree. This again explains why the high number direct cotton dyestuffs give the most level results.

The following simple test enables one to select the most suitable direct cotton dyestuffs for viscose from this point of view.

Dye two equal weights of viscose at the same time in the same dyebath, then boil in a fresh bath with 2 per cent. soap on weight of material for half an hour one of the dyed pieces of viscose with an equal weight of undyed viscose. It will be found that the high number direct cotton dyestuffs boil off the dyed viscose and dye the undyed viscose to approximately equal depth of shade ; in other words, a state of equilibrium is reached in the boiling soap bath, so that both dyed and undyed viscose are of the same depth of shade.

Under the same test the low number direct cotton dyestuffs lose much less depth of shade and the undyed viscose will be left practically unstained.

If this test is applied to any compound shade dyed with three direct cotton dyestuffs, it will demonstrate very clearly the suitability or otherwise of the dyestuffs used. If a compound shade of brown when submitted to this test loses the black and yellow portion, whilst the red portion does not boil off, it is a very clear indication that the red is the faulty component.

It will be seen that each of the above three tests supplements and confirms the others, and shows in a clear and definite manner the suitability or unsuitability of direct cotton dyestuffs for the dyeing of viscose.

It is an unfortunate fact that there are some gaps in the direct cotton series of suitable dyestuffs for certain shades, notably blues and greens, but some dyestuff manufacturers are conducting research work to fill the gaps and have already been successful in some cases.

4. Experience has also shown that the high number dyestuffs for viscose require the addition of the least Glauber's or common salt to exhaust the dyebath, whilst the low number dyestuffs require a considerable addition of Glauber's salt to get value out of the dyestuff. From the point of view of evenness, it is therefore advisable to omit Glauber's salt whenever possible ; this may be done with high number dyestuffs with very little additional cost in dyestuffs, which is quickly balanced by the much improved results obtained. When using low number dyestuffs, such as Sky Blue FF, it is not practicable to dispense with Glauber's salt, since it is impossible to obtain adequate value from the dyestuff without this assistant, thus giving an additional reason why high number dyestuffs give superior results to low number dyestuffs.

5. Viscose should always be dyed with direct cotton dyestuffs at as high a temperature as circumstances permit. Viscose itself may be dyed at the boil without any detriment to its lustre or strength. All direct cotton dyestuffs—whether high or low number—give their most even results at high temperatures. The viscose should be immersed in the dyebath at a high temperature.

An alternative to the usual method of dyeing viscose with soap or soluble oil and Glauber's salt, is to dye with the addition of Monopol soap or Monopol brilliant oil in conjunction with formic or acetic acid. This will frequently be found to give the more even results, particularly in the case of many direct cotton blues and greens as self shades or in combination with direct cotton yellows.

HYDRO-EXTRACTORS

By permission of BRIAN L. BROADBENT

TEXTILE fabrics of all kinds, after they have passed through the washing, scouring, and milling machines, or dyebaths, contain a large amount of water, often exceeding in weight that of the fabric itself, and to take these goods direct from the preceding operations to the drying plant would mean that a prohibitive amount of fuel and time would have to be expended to dry out this vast amount of water. It is most desirable for the goods to be freed from as much of this excess water as possible before they are put into the drying chambers, and this may be done in three ways—by squeezing or wringing, by mangling, or by hydro-extracting. Of these three methods, hydro-extracting is the most important, and will receive most attention.

Mangles are never used for wool or silk fabrics, but are occasionally adopted for cotton fabrics, which can be mangled in open width. Knitted fabrics of any class of materials are never mangled. Mangles are generally provided with two or three rollers, and are somewhat similar in construction to the squeezing rollers previously described, except they have no traverse motion, and have flat rollers, usually of brass or wood, and wide enough to accommodate fabric in open width. Pressure on the rollers is obtained by means of levers and weights.

HYDRO-EXTRACTORS

Hydro-extractors have proved to be by far the best machines that have yet been devised for expelling the bulk of moisture in hanks
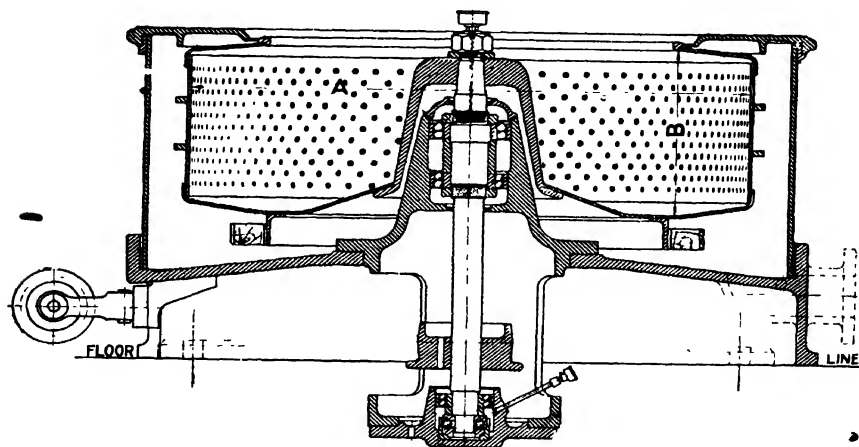
FIG. 118.—SECTION OF HYDRO-EXTRACTOR.

and fabrics of all kinds. They have stood the test of time, and are adopted as standard practice throughout the whole of the textile industry and allied trades. A hydro-extractor, sometimes called a "centrifugal drier" or "whizzer," consists of a perforated cage or basket, mounted on a vertical spindle, and enclosed within an outer case, as shown in Fig. 118, leaving the top portion of the cage accessible. The wet material is placed inside the cage, which is then revolved at very high speed by means of a belt, steam engine, electric motor, or other means. This process subjects the wet material to great centrifugal force, which draws the water from the material out through the perforations in the cage into the outer case, from which it drains away, and the dried material is retained within the cage.

Although more often used for loose materials and woven or knitted fabrics, hydro-extractors can be used for hanks, cops, cheeses, etc., as the centrifugal action keeps these in position while being " whizzed."

Hydro-extracting produces a more uniform dryness than can be obtained by any other mechanical process, and the uniformity is always constant for every varying class of material. Moreover, the texture of the material is in no way damaged by pressure, and
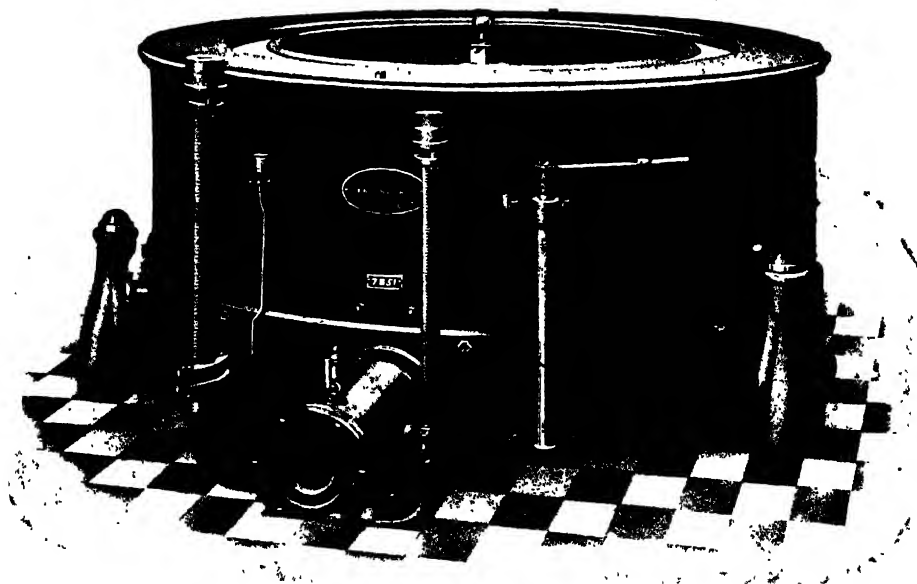
Fig. 119.—48-in. Steam-driven Hydro-Extractor.

the most delicate fabrics can be treated with perfect safety. In hydro-extracting the water is drawn out of the material by centrifugal force, which is entirely different from squeezing it out by pressure, as in the case of squeezing and wringing machines.

Steam-driven Hydro-Extractors. Fig. 119 shows a 48-in. direct steam-driven, suspended, hydro-extractor. This type of machine was very widely used in the days before the advent of electricity, and is still very popular in factories where electricity is not available. These machines are direct-driven by a small steam-engine attached to the casting forming the base of the outer case. They have the advantage of exceedingly quick acceleration, but on account of the reciprocating motion wear and tear is liable to be excessive, and, consequently, maintenance costs are usually higher than in the

other methods of driving. Moreover, these machines, containing, as they do, so many working parts, require a deal of supervision, and should be periodically examined to see that lock-nuts have not become loose, bearings or bushes worn, etc. Systematic inspection of these machines saves many a costly breakdown.

The engine is of the ordinary single-cylinder type, with a flat slide-valve set at about one third cut-off. It will work at any steam pressure from 30 lb. per sq. in. upwards, but, of course, the higher the pressure the quicker the acceleration will be. At 80 lb. pressure, the hydro-extractor will attain full speed in less than one minute. The steam and exhaust connections to the cylinder have
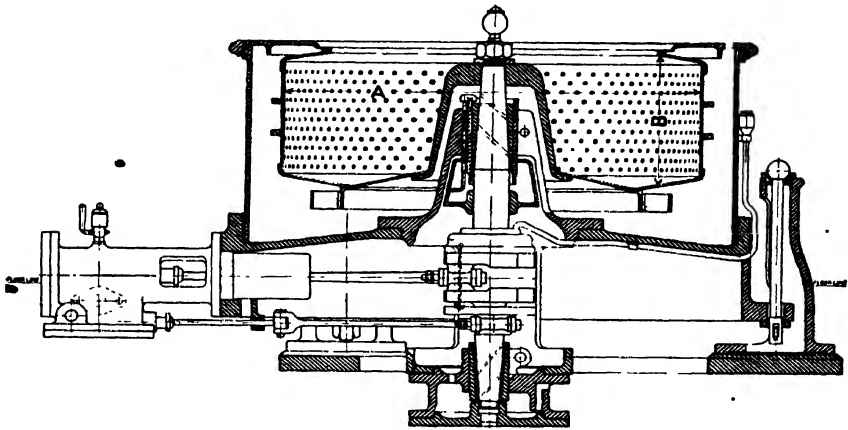
Fig. 120.—Section of Steam-driven Hydro-Extractor.

to be flexible pipes to allow for the oscillation of the machine, and it is most desirable to arrange for the exhaust-pipe to have a downward fall from the engine, to enable condensed water to drain away. The cylinder is provided with a drain-cock, which should be opened before the engine is started up, if this has been standing for a few hours, otherwise there is a danger of the cylinder end being broken due to water accumulating in the cylinder.

Machines of this type have taper gun-metal bearings both top and bottom, as shown in Fig. 120, and a hardened steel footstep at the bottom of the spindle, which supports the entire weight of the cage. These taper bushes allow slackness due to wear to be taken up quite easily by unscrewing the lock-bolt and tightening the outer bush. Owing to the reciprocating motion, steam-driven hydro-extractors are not fitted with ball bearings, as is usual with other types of machines.

A rather unique feature is the lubricating arrangement for the

crankpin and eccentric, which is entirely automatic. A small charge of oil is trapped each time the machine is started-up, and this oil lubricates these parts when the machine stops ready for the next start. For this reason it is advisable not to run steam-driven machines longer than 20 minutes continuously. With this system of lubrication there is no waste of oil when the machine is standing.

This machine, and most of the other machines described later, is suspended on three short columns by means of hanging bolts with spherical ends. This suspension arrangement was patented by the late Thomas Broadbent, 52 years ago, and is still adopted as modern practice for under-driven machines by almost every hydro-extractor maker throughout the world. Although this arrangement is simplicity itself, it has a very important bearing upon the running of the machine, as it allows flexibility and permits the loaded cage to rotate round the new centre of gravity during acceleration and while running. This three-point suspension enables the machine to run quite sweetly even with a reasonable out-of-balance load in the basket, which would otherwise cause violent vibration. Moreover, it relieves the spindle of all undue stress and minimizes the wear on the spindle bearings.

As all movement is absorbed by the suspension bolts, no vibration is communicated to the ground, consequently the foundations need only be of small proportions, thereby reducing the cost of installation.

The direct-coupled engine drive can only be applied to suspended type machines, as it is impossible to balance a single-cylinder of this type, and, consequently, an out-of-balance load, due to the engine alone, is always created.

ELECTRICALLY-DRIVEN HYDRO-EXTRACTORS

In the first place, this machine has an entirely unobstructed passage all around the outer case, as shown in Fig. 121. This is a great convenience for working arrangements, as the cage can be loaded or unloaded at any point, and a truck can be run alongside any part of the machine. There is also the convenience of being able to run the machine at any time, even if the main power plant is standing, also the simplicity of manipulation.

The absence of belts eliminates the annoyance of broken belts, belts slipping off the pulleys, periodical tightening-up of belts, replacement of belts, etc. There are no steam joints to break, piston and valve rods to pack, or constant lubrication of working parts. There is no engine noise, or an atmosphere of escaping steam due to the joints and packings not being tight, etc.

Electrically-driven machines occupy very little floor-space, and, owing to an entire absence of reciprocating parts and the introduction of roller bearings throughout, they run almost noiselessly and with very little attention.

As indicated in Fig. 122, the electric motor is an integral part of the machine. The rotor revolves around the centre spindle, which carries the cage, and the stator is built on to the framework. There is, therefore, no complicated mechanism of any kind, and all movement is rotary. Because of the fewness of parts subjected to excessive vibration, friction or wear, this type of machine is very durable.

Hydro-extractors take more starting than almost any other class of machine, and require a motor which will give an exceptionally high starting torque with a reasonably low starting current.
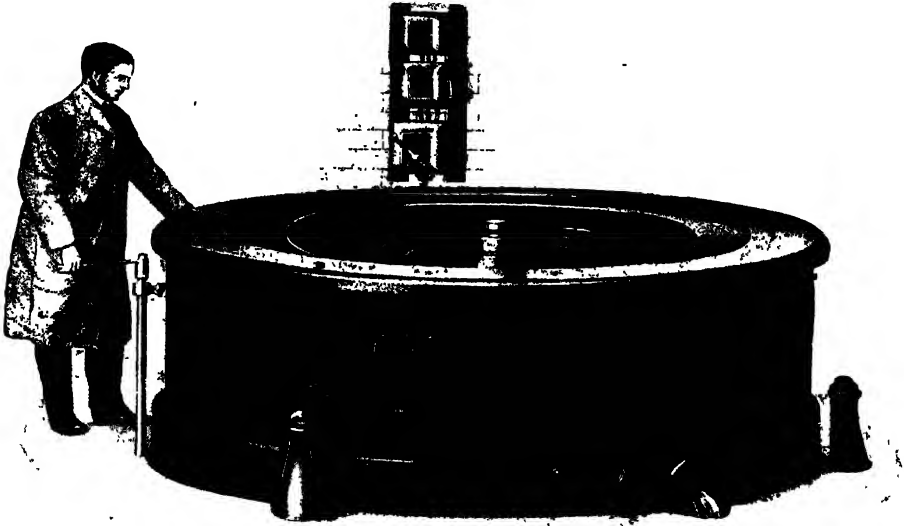
FIG. 121.—72-IN. DIRECT ELECTRICALLY-DRIVEN SUSPENDED HYDRO-EXTRACTOR.

It must be of very robust construction, owing to rough handling, mainly by unskilled workers, and also of high rating to withstand frequent starting.

The motor is not coupled direct to the cage spindle, but drives through a centrifugal clutch, containing loose friction shoes, and is similar in principle to the one used for belt-driven hydro-extractors as previously described. This arrangement consists in the mounting of the armature or rotor upon an independent sleeve, which can revolve round the cage spindle. To the upper part of the sleeve is attached friction shoes, which are thrown outwards by centrifugal force when the armature or rotor commences to rotate and engage with the inside rim of the clutch keyed to the cage spindle. The

hydro-extractor is thus gradually brought up to its proper running speed without excessive current consumption, although the armature or rotor is running approximately at its full speed the whole of the time. The advantages of this arrangement are—

1. The starting up of the machine is quite automatic.

2. The attendant cannot damage the motor by switching on the current too suddenly.

3. The starting current never exceeds a maximum figure, which can be definitely fixed when designing the machine.

4. The drive becomes positive after about 75 per cent. of full speed has been attained.
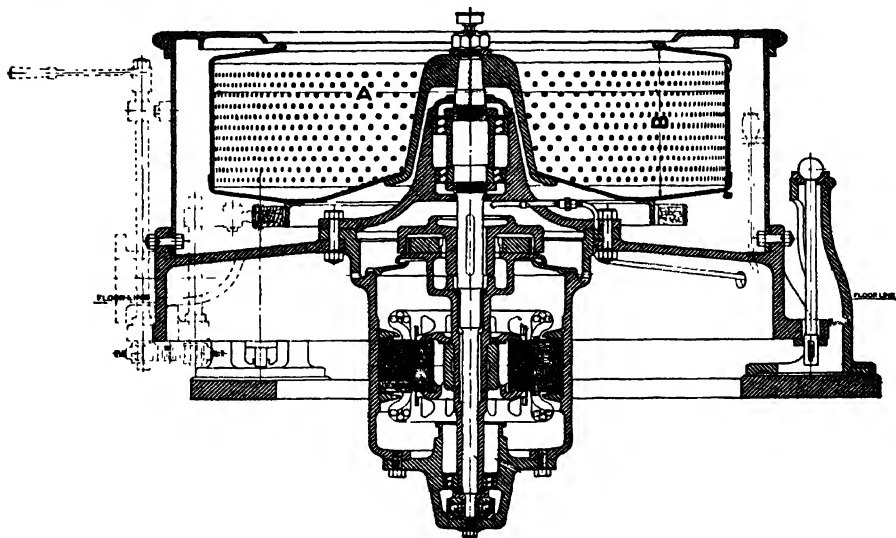
FIG. 122.—72-IN. DIRECT A.C. ELECTRICALLY-DRIVEN SUSPENDED HYDRO-EXTRACTOR.

Acid Resisting Cages. A very popular type of cage is made from mild steel and coated with vulcanite. These are splendid acid-resisting cages, and are to be highly recommended. Moreover, they have an exceptionally smooth finish, and are very often used for delicate fabrics, such as artificial silk, on account of this advantage. It is very desirable for cages of this kind to be coated with the best quality of vulcanite, otherwise they are soon liable to crack. Vulcanized cages will not stand great heat, consequently they are no use for hydro-extracting very hot materials.

Deep cages are very advisable in cases where they are required for drying granular substances which can be discharged by gravity out of the bottom of the cage, but for textile goods, which have to

be put in and taken out by hand at the top of the cage, the convenience of shallow cages is indisputable. Shallow cages allow a man to lean over the machine and reach the bottom with very little effort or stretching of arms. Consequently, they are not as fatiguing to the men, and the machines are loaded and unloaded much more rapidly, thereby increasing output.

Acid machines, that is machines with copper or vulcanized-steel cages, usually have their cases completely lined in the interior with chemically-pure sheet lead to prevent corrosion. This will give a long number of years' service, but ought to be inspected occasionally, and any sign of deterioration immediately patched up, or any opened joints resoldered, otherwise the corrosion will spread very rapidly.

Speed. The speed of a hydro-extractor depends upon the diameter of the cage, and consequently the speed of each size of machine varies. The safe speed is entirely dependent upon the strength of the cage shell, and no great advantage is derived by increasing the thickness of this. The weight of the shell itself has to be taken into account, and even in an unloaded cage there is a certain surface speed at which bursting will occur, which is independent of the thickness of the shell or its diameter.

The total stress on the shell is the sum of the self stress and that due to the radial pressure of the load. For steel cages the total stress on the metal should not exceed 6 tons per sq. in., and for copper cages 3 tons per sq in.

SPEEDS AND GRAVITY FACTORS OF HYDRO-EXTRACTORS

Dia. of Cage	Revs. per Minute	Gravities	Dia. of Cage	Revs. per Minute	Gravities
In.			In.		
2	40,000	45,300	36	1000	512
4	17,000	16,400	42	950	538
5	10,000	7,100	48	900	553
9	2,400	735	54	800	490
18	1,500	575	60	750	479
21	1,300	505	72	650	432
26	1,200	530	84	500	300
30	1,150	565			

In a 72-in. machine, at 650 r.p.m., giving an extraction force of 432, the surface speed of the rim is 12,242 ft. per min., while a 36-in. machine, at 1000 r.p.m., gives an extraction force of 512 and a surface speed of 9418 ft. per min.

Power. A hydro-extractor usually takes about two-and-a-half times more power to start it from rest than to run it. This extra starting torque, however, is only required for the first few seconds.

After acceleration has commenced, the power requirements rapidly fall down to a normal amount required to maintain the running of the machine at full speed.

Belt-driven Hydro-Extractors

Where direct steam or motor power is not available a belt-driven machine is a very acceptable type, as it can be driven direct, as illustrated in Fig. 123, which represents a 42-in. belt-driven hydro-extractor. This type is usually on the small size, but they can be made in larger sizes.

In the suspended type machines they are invariably driven from an overhead countershaft. This countershaft has fast and loose pulleys to enable the machine to be started and stopped by means of pendant cords, and is provided with a centrifugal clutch pulley. The belt is led vertically from the clutch pulley over jockey pulleys fixed on the side of the machine to the pulley on the cage spindle.

This centrifugal clutch pulley is a very important feature and worthy of a little consideration. In starting-up a hydro-extractor various resistances have to be overcome, the chief of which is the inertia of the basket and load. There is also the bearing resistance and the air resistance, both of which increase with the speed. If the machine had to be started-up from a solid pulley on the countershaft, these resistances would cause the belt to slip for a very considerable time before picking up the load, consequently the wear on the belt would be abnormal, and new belts would be very frequently required.

It is to eliminate this trouble, therefore, that the centrifugal clutch pulley is embodied. This clutch is comprised of two parts, an interior spider keyed on to the countershaft and an outer belt pulley running loosely on the spider sleeve. The spider has four pockets, each containing a loose shoe lined with " Ferodo," and immediately the countershaft is put into motion these shoes are thrown radially outwards by centrifugal force, and press against the interior rim of the belt pulley. As the speed of the countershaft increases, the pressure of the shoes increases until this is sufficient to put the best pulley into motion, and enable it to start-up and drive the machine.

By means of these slipping shoes, the hydro-extractor is very gradually brought up to full speed without any belt slip, and without any sudden jar or shock. When the machine attains full speed all slip in the clutch ceases, and the drive becomes positive as in a solid pulley.

This form of clutch has now become exceedingly popular for motor-driven textile machines of almost every description, such as ring frames, scutchers, looms, lineshafts, etc. It is now becoming quite the usual practice to fit centrifugal clutch pulleys or couplings

FIG. 123.—42-IN. BELT-DRIVEN HYDRO-EXTRACTOR.

to electric motors of all types, because of the smooth and easy starting that is ensured.

With belt-driven machines, ball or roller bearings are used, as there is no reciprocating action as with engine-driven machines. There is still, however, the loss of efficiency due to the belt-drive, together with the maintenance cost of the belt, which puts this type of machine into rather a low category.

A suspended type of belt-driven machine that is now becoming popular is that with a self-contained countershaft carried on an extended bed-plate. In cases where there is a limited head-room for the countershaft this is a very useful type of machine, and, moreover, it makes the countershaft very accessible for lubrication purposes. It is quite impossible with suspended type machines to have the belt pulling in a horizontal direction, as this would cause violent oscillation, therefore the belt must always drive vertically.

Hydro-extractors with a horizontal drive can be arranged, as in a case where there is no line-shafting or no accommodation for a countershaft. It is possible to drive machines of this type from a motor or countershaft placed at the floor level, but if this is done, a bolted-down machine would have to be used, and, as previously stated, bolted-down machines should be avoided if at all possible in the treatment of textile fabrics.

DRYING EFFICIENCIES

A hydro-extractor dries by intensifying gravity force by means of centrifugal action, and the amount of centrifugal force applied is more or less determined by the speed. There are some very interesting points, both with regard to speeds and the length of time centrifugal force can be usefully applied, which may now be considered.

The table shown on page 297 has been compiled by the Chemical Department of the Northern Polytechnic Institute. These figures were determined after prolonged experiments by experts, and show the apparent efficiency (per cent.) of a hydro-extractor.

These figures will, of course, vary a little according to the gravity factor of the machine and the material dealt with. Although the experiments were carried out on chemical crystals they will serve to illustrate a few certain facts.

    1. That the length of time the material is " whizzed " is of no advantage after a certain period.

    2. That increased speed above a certain amount is not of very great importance.

" *Whizzing* " *Time.* At a speed of 1,198 r.p.m. the efficiency is 71·7 after the first 5 mins., whereas after 15 mins. this has been increased to only 73·5. Thus by increasing the length of running

APPARENT EFFICIENCIES OF HYDRO-EXTRACTORS

| Mins. | 100 | 124 | 197 | Speed, r.p.m. | | | 602 | 697 | 1198 |
				330	368	476			
0·5	—	—	—	—	—	10·0	14·2	18·0	35·0
1·0	—	—	—	13·1	15·8	20·1	25·0	46·5	55·3
2·0	—	—	18·5	24·5	29·6	34·4	46·7	50·0	65·4
3·0	—	9·4	25·0	31·1	37·1	43·0	56·1	64·5	69·2
4·0	—	—	30·8	36·7	44·3	48·4	60·8	67·0	70·5
5·0	—	13·4	34·9	40·3	48·6	52·4	63·0	68·9	71·7
7·5	—	17·4	40·4	49·9	57·0	59·8	66·8	70·5	72·0
10·0	7·2	20·4	44·8	56·5	60·8	66·5	69·3	71·1	72·5
15·0	10·8	27·6	52·5	64·8	68·6	70·6	70·9	71·4	73·5

time by 10 mins. the extra drying efficiency has been increased only by 1·8 per cent. After five minutes' run practically the whole of the water has been extracted, and the slight increase in efficiency is no doubt due more to the air circulation through the material than to longer " whizzing."

Speeds. With regard to increase of speeds, a five-minutes' run may be considered. At 1,198 r.p.m. the efficiency is 71·7, and at 697 r.p.m. the efficiency is 68·9. Therefore, increasing the speed an additional 500 r.p.m. has increased the efficiency by only 2·8 per cent. This proves that the slight additional drying obtained from high-speed machines or long durations of run is not worth the extra power cost, the additional wear and tear, and loss of time and output.

Artificial Silk. Most of the foregoing remarks are of general application, but the following refer directly to the treatment of artificial silk. Viscose silk of 300 deniers in small hanks contained 181 per cent. of water after being wrung by hand on leaving the dye vat. After 10 mins. hydro-extracting the residual moisture was reduced to 78 per cent. It is usual to wrap the artificial silk in strong cotton cloths and place bundles of these all round the periphery of the cage. This prevents any possible damage to the artificial silk due to rubbing against the side of the cage.

It is also advisable to pack the machine round the periphery only, and not completely fill the cage. The water is thus thrown out of the artificial silk direct into the outer case, and has not to drain through a cage full of material, as in the case of wool or cotton drying, when the cage is filled to its utmost capacity. The most usual size of machine for artificial-silk drying is 48 in. diameter, but machines up to 60 in. are occasionally used.

While the machine is running there is always a circulation of air

passing from the cage and through the spout, and this air current carries with it particles of water from the outer cases for some considerable time, even after the drying has been actually completed. The duration of time the machine should be run depends entirely upon the class of material it is drying, and users of these machines ought to make a special study of this particular point.

Immediately what might be termed the " commercial dryness " has been attained, it is both a loss of time and output and waste of power to continue running the machine until the " possible dryness " is attained. It would be very advisable for users of hydro-extractors to carry out a few simple tests on their own particular materials or fabrics and determine the time these ought to be run. They could then adopt these times as their own standard practice, and give the hydro-extractor men definite instructions not to exceed them. In some factories it is usual to allow the men to stop the machine entirely at their own discretion, and consequently they stand by and run the machine far longer than necessary.

Another question often asked is : " What pressure per square inch is exerted on the material during hydro-extracting ? " The pressure can be calculated if the load in the cage is a definite solid mass, like water, for instance. Thus, assuming a drum 60 in. diameter, running at 750 r.p.m., contained a wall of water 4 in. deep, the pressure exerted on the outer shell would be 65 lb. per sq. in. Increasing the depth of the mass would increase the pressure, and if the drum were filled up to the edge of the lip, thus giving a depth of $6\frac{1}{2}$ in. of water, the pressure would be increased to 100 lb. per sq. in.

With a load of textile goods, however, no definite mass can be ascertained, as this does not pack solid and the thickness of the load is constantly varying during hydro-extracting. The efficiency of a hydro-extractor, therefore, is invariably expressed as a gravity factor as previously described, and pressures are rarely taken into account.

Although all the hydro-extractors illustrated are used extensively in nearly all classes of trades, it will be evident that, in the case of piece goods, the cloth will certainly be creased. In most instances, subsequent finishing machines can remove these creases quite satisfactorily, but, in other instances, it may be desired to prevent their appearance as much as possible at every stage. For the latter instances, it is advisable to use the new horizontal hydro-extractor recently developed by Messrs. Thomas Broadbent & Sons, Ltd., Huddersfield, who are the sole makers of this type of machine.

The machine, which is illustrated in Fig. 124, has a perforated drum, 62 in. long by 30 in. diameter, shown immediately under the elevated outer case or cover. The drum is hollow, and as it rotates provision is made for a current of air to circulate through the material. It will be understood that the cloth is wound on the

perforated drum immediately before the operation of hydro-extracting commences. The power for winding the cloth on to the perforated drum is supplied by a special motor, and the cloth is made to run without creases on to the perforated drum by a suitable tension roller ; in this way the cloth is wound evenly upon the drum.

When all is ready, the large cover is lowered to enclose the perforated drum, which is also driven by a special motor. The perforated drum rotates at 960 r.p.m., and the water from the cloth is
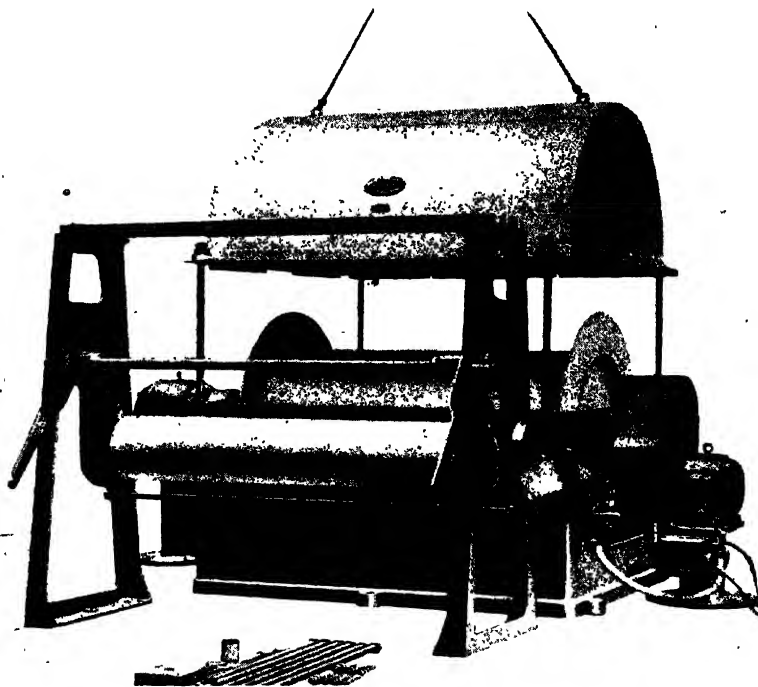
FIG. 124.—BROADBENT HORIZONTAL HYDRO-EXTRACTOR

thrown off in virtue of the high centrifugal force against the walls of the above-mentioned outer cover, from which it is drained away by means of an outlet pipe at the bottom.

The work done by the machine has already exceeded expectations, as the following satisfactory test should prove. A union fabric, cotton warp and "Celanese" weft, 480 ft. long, and 36 in. wide, was treated in a 30 in. diameter machine.
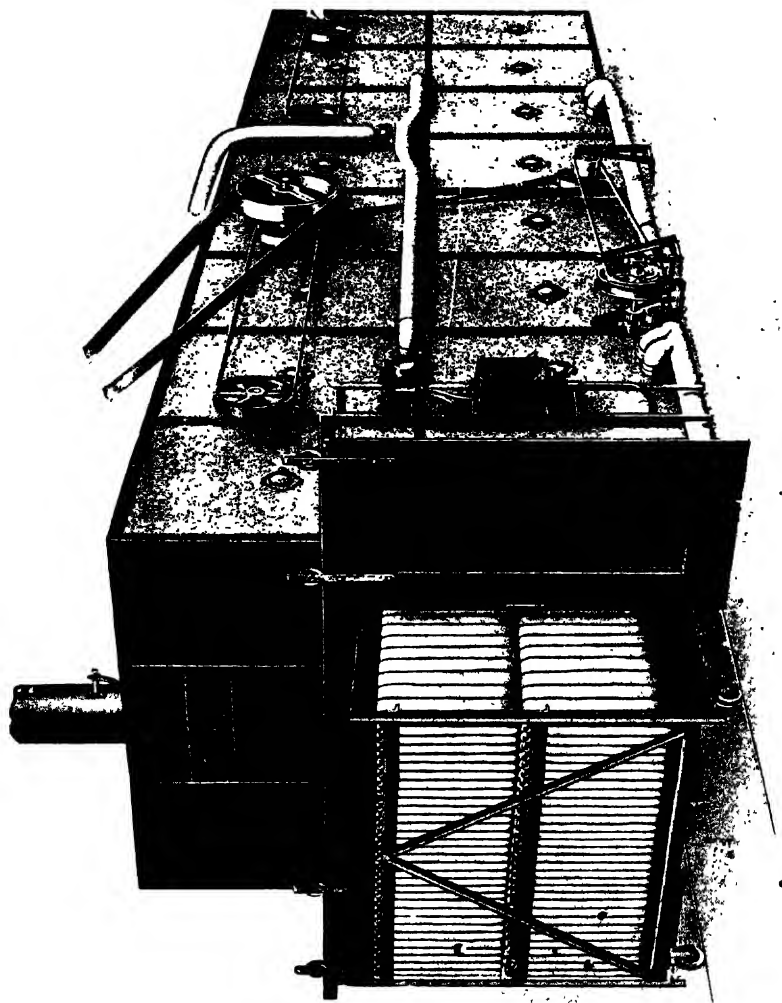
FIG. 125

Average winding-on speed   = 175 ft. per min.
Weight of piece after the hydro-extracting operation = 69 lb.
Final dried weight of piece   = 46 lb.
Percentage of moisture remaining in piece after hydro-
   extracting   = 33½%.
Length of run = 5 minutes from closing electric switch to opening the
    switch and applying the brake.

The efficiency of the hydro-extractors is universally recognized, but it is always understood that a subsequent drying operation is necessary before the yarn or cloth is properly conditioned. As a matter of fact, it is considered advisable in many cases to dry the hanks twice after they leave the spinning department.

The first of these two drying operations is termed " stoving " or " tight drying," whereas the second operation is known as " loose drying " or " white drying." The term " tight drying," which is employed by the many artificial silk manufacturers, involves the use of stretcher frames, by means of which the hanks are stretched immediately before they are stoved or dried. On the other hand, other manufacturers omit this stretching operation.

The artificial silk from the spinning room contains approximately five times its weight of water, and much of this moisture is removed in the hottest chamber of the drying machine, in which chamber a temperature of 190° F. is registered. The remaining chambers have temperatures of 160°, 130° and 110°. Approximately 10 per cent. of the wet-reeled length of yarn is lost by shrinkage during the operation of stoving, which may take place either in a chamber machine or in a tunnel machine such as that illustrated in Fig. 125. Both types are made by Messrs. Tomlinsons (Rochdale) Ltd.

The yarn is rather harsh after it is withdrawn from the stoving frame, particularly if sulphur is present, and the threads show a tendency to stick together ; a satisfactory separation, however, often takes place during the desulphurizing process, which is conducted between the first and second drying operations. The first desulphurizing bath takes place at a temperature of 150° F., and if the threads still adhere to each other, they might be separated during the loose drying.

The desulphurizing, acidifying, bleaching, and washing operations are invariably followed by the foregoing process of hydro-extracting, after which the hanks are ready for being sorted, packed, and dispatched to the users.

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